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METHOD STUDY 2: NUTRIENT ANALYSES,
MANUAL METHODS

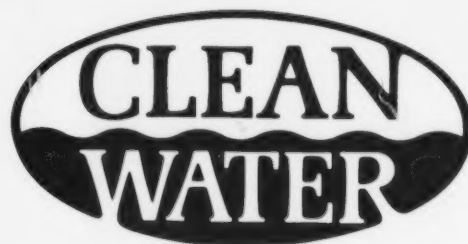
Federal Water Pollution Control Administration
Cincinnati, Ohio

1970

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ENVIRONMENTAL PROTECTION AGENCY
Water Quality Office
Analytical Quality Control Laboratory
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An Evaluation of Analytical Methods for Water and Wastewater

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METHOD STUDY 2, NUTRIENT ANALYSES,

MANUAL METHODS

An Evaluation of Analytical Methods for Water and Wastewater

J. A. Winter and M. R. Midgett

ENVIRONMENTAL PROTECTION AGENCY
Water Quality Office
Analytical Quality Control Laboratory
1014 Broadway
Cincinnati, Ohio 45202

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ACKNOWLEDGEMENTS

The authors acknowledge the technical assistance and guidance of Mr. Elmo C. Julian, Analytical Quality Control Laboratory, in the design, development and operation of the statistical and graphical computer programs used in this study.

PARTICIPATING LABORATORIES

Forty-nine analysts in twenty-two laboratories took part in *Method Study 2, Nutrients*. Of these, three were non-Water Quality Office (WQO) laboratories. The participating laboratories were:

WQO Laboratories

Alaska Water Laboratory
College, Alaska

California/Nevada Basins
Sub-Region
Alameda, California

Chesapeake Technical Support
Laboratory
Annapolis, Maryland

Colorado River/Bonneville
Services Branch
Salt Lake City, Utah

Division of Field Investi-
gations
Cincinnati, Ohio

Hudson-Delaware Basins Office
Edison, New Jersey

Joint WQO-DC Pilot Plant
Washington, D.C.

Lake Huron Basin Office
Grosse Ile, Michigan

Lake Michigan Basin Office
Chicago, Illinois

Lake Ontario Basin Office
Rochester, New York

Lower Ohio Basin Office
Evansville, Indiana

New England Basin Office
Needham Heights, Massachusetts

Missouri Basin Laboratory
Kansas City, Missouri

Pacific Northwest Water Laboratory
Corvallis, Oregon

R. S. Kerr Water Research Center
(Technical Programs)
Ada, Oklahoma

R. S. Kerr Water Research Center
(Research Program)
Ada, Oklahoma

Shagawa Lake Eutrophication Control
Pilot Project
Ely, Minnesota

Southeast Water Laboratory
Athens, Georgia

Upper Ohio Basin Office
Wheeling, West Virginia

Non-WQO Laboratories

Solid Wastes Office, EPA
Cincinnati, Ohio

California Division of Water
Resources Regional Laboratory
San Bernardino, California

Washington Pollution Control
Commission
Olympia, Washington

METHOD STUDY 2, NUTRIENT ANALYSES, MANUAL METHODS

An Evaluation of Analytical Methods for Water and Wastewater

SUMMARY

The Analytical Quality Control Laboratory of the Water Quality Office, EPA, formerly Federal Water Quality Administration, conducted interlaboratory studies on selected chemical methods of analysis for ammonia nitrogen, nitrate nitrogen, Kjeldahl nitrogen or organic nitrogen, orthophosphate and total phosphorus. Samples were prepared in pairs at similar yet different concentrations for each constituent. Analysts added an aliquot of each concentrate to distilled water and to a natural water of their choice. Single analyses were made on the distilled and natural water samples with and without added increments. Recoveries were compared and the bias of the method, the interference of natural water samples and the relative precision of each analyst and laboratory were determined. On pages *vi* and *vii* a statistical summary of this data shows the precision and accuracy values which may be expected in routine work.

A Statistical Summary of Method Study 2,

Nutrient Analyses, Manual Methods

Ammonia Nitrogen Analyses of Natural Water Samples				
True Value, mg N/liter	.26	.21	1.71	1.92
Mean of Recoveries by Difference, mg N/liter	.21	.22	1.75	1.96
Accuracy as % Relative Error (Bias)	-18.12	-5.54	.46	-2.01
Standard Deviation, mg N/liter	.07	.12	.24	.28
Range, mg N/liter	.30	.63	1.01	1.17

Nitrate Nitrogen Analyses of Natural Water Samples				
True Value, mg N/liter	.16	.19	1.24	1.08
Mean of Recoveries by Difference, mg N/liter	.16	.20	1.25	1.16
Accuracy as % Relative Error (Bias)	-6.79	8.30	2.82	4.12
Standard Deviation, mg N/liter	.09	.08	.21	.24
Range, mg N/liter	.46	.33	1.01	1.44

Orthophosphate Phosphorus Analyses of Natural Water Samples				
True Value, mg P/liter	.029	.038	.383	.335
Mean of Recoveries by Difference - mg P/liter	.027	.036	.374	.326
Accuracy as % Relative Error (Bias)	-4.95	-6.00	-1.76	-2.75
Standard Deviation, mg P/liter	.010	.008	.023	.018
Range, mg P/liter	.046	.036	.126	.071

Statistical Summary, Contd.

Kjeldahl Nitrogen - Organic Nitrogen Analyses of Natural Water Samples				
True Value, mg N/liter	.31	.20	4.10	4.61
Mean of Recoveries by Difference, mg N/liter	.33	.23	4.14	4.53
Accuracy as % Relative Error (Bias)	5.45	15.54	1.03	-1.67
Standard Deviation, mg N/liter	.25	.20	1.06	1.19
Range, mg N/liter	1.05	.77	3.97	4.71

Total Phosphorus Analyses of Natural Water Samples				
True Value, mg N/liter	.110	.132	.882	.772
Mean of Recoveries by Difference, mg P/liter	.121	.155	.890	.813
Accuracy as % Relative Error (Bias)	3.09	11.99	-.92	2.96
Standard Deviation, mg P/liter	.033	.051	.129	.130
Range, mg P/liter	.167	.318	.765	.777

METHOD STUDY 2, NUTRIENT ANALYSES, MANUAL METHODS

An Evaluation of Analytical Methods for Water and Wastewater

INTRODUCTION

The Water Quality Office, EPA, formerly Federal Water Quality Administration, gathers water quality data to determine compliance with water quality standards, to provide information for planning of water resources development, to determine the effectiveness of pollution abatement procedures, and to assist in research activities. In a large measure, the success of the pollution control program rests upon the reliability of the information provided by the data collection activities.

To insure the reliability of physical, chemical, biological and microbiology data, the Division of Water Quality Research established the Analytical Quality Control (AQC) Laboratory, at 1014 Broadway, Cincinnati, Ohio. The AQC program, conducted by this laboratory, is designed to assure the reliability, and when necessary, the legal defensibility of all water quality information collected by the Water Quality Office.

The Method and Performance Evaluation (M&PE) Activity of the AQC Laboratory conducts evaluative interlaboratory studies of analytical procedures selected for use in WQO. In this study the nutrient parameters were examined to obtain the accuracy and precision of the selected manual methods used in the participating WQO laboratories. The evaluation of results also permits a judgment of the relative capabilities of these laboratories performing these analyses.

DESCRIPTION OF THE STUDY

Test Design

Youden's non-replicate technique of x and y samples (1) is used in a test design as follows:

1. Each sample is prepared as a stable concentrate in a sealed glass ampul.
2. As many sample constituents as possible are combined in a single ampul.
3. Using Youden's x-y sample technique, similar yet different samples are prepared and analyzed once only.
4. When an aliquot of the concentrate is diluted to volume, all constituents are present at levels found in natural waters.
5. Several levels of concentration are tested to cover the normal levels found in surface waters.
6. Each of the x-y sample pair is added independently to a distilled water and natural water of choice and samples analyzed. The distilled and natural waters are analyzed with and without increments.

Recoveries are compared.

Preparation of Samples and Reporting of Results

Eight water sample concentrates were prepared for Method Study 2 by dissolving weighed amounts of reagent-grade chemicals in ASTM reagent-grade distilled water to produce accurately-known concentrations of ammonia, nitrate, total Kjeldahl nitrogen, orthophosphate and total phosphorus.

The distilled water, natural water spike technique was used in this study. Each analyst was instructed to dilute a separate 5.0 ml aliquot

of each concentrate to one liter with ammonia-free distilled water and a river, lake, or estuarine water. For each constituent, a result was obtained for: (1) the distilled + increment, (2) the natural water, and (3) the natural water + increment. Recovery of the increment in natural water was determined by difference.

The concentrates were preserved to prevent biological activity, and were checked for stability by repeated analyses over a period of three months. These analyses established that the solutions were stable, and verified the concentration of each constituent. Further confirmation of the true values was obtained from determinations by an independent referee laboratory. The true values are shown in Table 1.

Table 1
True Values for Parameters*

When diluted in distilled water according to instructions, the water samples contained the following concentrations of constituents, mg/l:

Ampul	NH ₃ -N	NO ₃ -N	PO ₄ -P	Kjeldahl-N	Total P
1	0.26	0.16	0.029	--	--
2	0.21	0.19	0.038	--	--
3	1.71	1.24	0.383	--	--
4	1.92	1.08	0.335	--	--
5	--	--	--	0.31	0.110
6	--	--	--	0.20	0.132
7	--	--	--	4.10	0.882
8	--	--	--	4.61	0.772

*The concentrations given in Table 1 are the actual levels present. These are not based on analyses, the latter being used only for verification.

Since dilution of the concentrates renders the preservative ineffective, it was necessary to analyze the ammonia and orthophosphate separately so that their values could not be increased by changes in the form of total Kjeldahl nitrogen or total phosphorus. Therefore, ampuls 1 thru 4 contained solutions for the ammonia, nitrate, and orthophosphate determinations while ampuls 5 thru 8 contained solutions for the total Kjeldahl nitrogen and total phosphorus analyses.

The set of eight ampuls covered two ranges of concentration for each measured parameter. Within each range, samples were paired, with each member of a pair: 1 & 2, 3 & 4, 5 & 6, and 7 & 8 being closely related in concentration.

The sample concentrates were shipped to participating laboratories on July 1, 1969. Detailed instructions for analyses and reporting of results were provided at that time.

Analytical Methods

The analyses were performed according to the *FWPCA Official Interim Methods for Chemical Analysis of Surface Waters*, September 1968 (2). The methods used for these manual analyses are as follows:

<u>Parameter</u>	<u>Method</u>	<u>Basic Reference</u>
Ammonia Nitrogen	Distillation	<i>Standard Methods for the Examination of Water and Wastewater</i> , 12th ed., APHA, Inc., N. Y., 1965, 187-193. <i>Book of ASTM Standards</i> , Part 23, 1967, Industrial Water; Atmospheric Analysis, pp. 336-338.
Nitrate Nitrogen	Modified Brucine Sulfate	<i>Standard Methods for the Examination of Water and Wastewater</i> , 12th ed., APHA, Inc., N. Y., 1965, 198-200. <i>Book of ASTM Standards</i> , Part 23, 1967, Industrial Water; Atmospheric Analysis, pp. 138-140.

Kjeldahl Nitrogen	Digestion	<i>Standard Methods for the Examination of Water and Wastewater</i> , 12th ed., APHA, Inc., N. Y., 1965, 402-404.
Orthophosphate	Single reagent	Murphy, J. and Riley, J. P., "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters," <i>Anal. Chim. Acta</i> , Vol. 27, 1962, pp. 31-36.
Total Phosphorus	Persulfate digestion and single reagent method	Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., "Method for Quantitative Determination of Total Phosphorus in Water," <i>JAWWA</i> , Vol. 58, No. 10, 1966, pp. 136-1368. Murphy, J. and Riley, J. P., "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters," <i>Anal. Chim. Acta</i> , Vol. 27, 1962, pp. 31-36.

Glossary of Terms

The statistical measurements used in this report are defined as follows:

Accuracy as % Relative Error (Bias). The signed difference between mean value and the true value, expressed as a percent of the true value.

$$\frac{x_{\text{true}} - \bar{X}}{x_{\text{true}}} \times 100$$

Confidence Limit (95%). The range of values within which a single analysis will be included, 95% of the time.

$$\bar{X} \pm t \frac{\sigma}{\sqrt{n}}$$

Mean. The arithmetic mean of reported values, the average.

$$\frac{\sum X}{n}$$

Median. Middle value of all data ranked in ascending order. If there are two middle values, the mean of these values.

n. The number of sets of values or analysts reported in a study.

Range. The difference in mg/l between lowest and highest reported values.

Relative Deviation (Coefficient of Variation). The ratio of the standard deviation, σ , of a set of numbers to their mean, $\bar{X}$, expressed as percent. It is an attempt to relate deviation (precision) of a set of data to the size of the numbers so that deviations between levels of values can be compared.

$$100 \frac{\sigma}{\bar{X}}$$

Skewness (k). A pure number, positive or negative, which indicates the lack of symmetry in a distribution. For example, k is positive if the distribution tails to the right and negative if the distribution tails to the left.

$$\frac{\sum (X_i - \bar{X})^3}{n\sigma^3}$$

Standard (σ) Deviation. The most widely used measure of dispersion of a set of data. It is equal to the square root of the variance and indicates the deviation of 68% of the values around the mean, and 2.58σ , the deviation of 99.7% of the values around the mean. σ , the *standard deviation*, is the measure of the deviation of the universe. However, in most experimental work with limited sampling and in this study only an *estimated standard deviation (s)* is measurable. This differs in calculation in that $n-1$ rather than n is used as the denominator. In this study and in further studies, s and s^2 not σ and σ^2 will be used to measure deviation of the data. They will be referred to as the *standard deviation* and *variance* respectively.

$$\sqrt{\frac{\sum X_i^2 - \frac{(\sum X_i)^2}{n}}{n}}$$

t-test. The difference in analyzed and true value expressed as ratio over the *standard deviation*. The value obtained is compared with critical values in a table. If the calculated t -value exceeds the theoretical t -value, the analyzed value is probably not from the same population as the rest of the data and can be rejected.

$$\frac{X_n - \text{true value}}{\text{Standard Deviation (s)}}$$

Variance (σ^2), (s^2). The average of the squares of the deviations of a group of numbers from their average, $\bar{X}$.

$$\sigma^2 = \frac{\sum X_i^2 - \frac{(\sum X_i)^2}{n}}{n}$$

$$s^2 = \frac{\sum X_i^2 - \frac{(\sum X_i)^2}{n}}{n - 1}$$

RESULTS

Raw Data

A direct copy of the computer printout of all test results reported by participant laboratories using manual methods is shown in Appendix 1 by parameter and by type of water sample. For the distilled water samples a simple listing is given of laboratories and analysts with their reported values. For the natural water samples, values were received for each analyst, but because spiking 995 ml of natural water with 5 ml of sample concentrate causes a 0.5% dilution change, the reported values were reduced by this amount. Differences between the natural sample values and the corrected (natural samples + spike) resulted in the corrected recovery values for natural water samples in the text and in Appendix 1. These corrected recovery values were used in all evaluations of data from natural waters. For ease in computer calculations and to avoid premature round-off errors, four digits were carried through all recovery calculations in the natural waters. Only two or three significant figures should be used for all final values based on the number of significant figures in the increment values.

Statistical Summary

A complete statistical summary is given in pages 12 thru 43. Each parameter is discussed in turn with data displayed in two-sample charts followed by statistical evaluations of the data for each concentration.

A program described by Larsen (3) was modified for an IBM 1130 computer and measurement of accuracy and presentation of ranked data were added. This summary presentation named COLST provides all of the statistical measurements necessary for evaluation of the data as a direct copy of the computer printout. With the exception of accuracy, all measurements: *number of values, true value, mean, median, accuracy, range, variance, standard deviation, 95% confidence limit, relative deviation* (coefficient of variation), and *skewness* are based on all data received, without rejection. *Accuracy*, is based on retained data, that is the data remaining after rejection of outliers using the *t-test* at the 99% level, because the inclusion of questionable extreme values will result in unreasonable values for accuracy. In addition to the statistical measurements, all data are ranked in ascending order and presented in a histogram, using a six cell division. Each X in the histogram represents one analytical result while the distribution of all X values characterizes the method as used on these natural water samples.

The precision and accuracy of WQO methods are derived from natural water data. For clarity and understanding, only the statistical summaries of the natural water data are given in the text with the two-sample charts for each parameter. The corresponding statistical summaries of the distilled water data are given in Appendix 2. Comparisons of the two-sample charts for natural and distilled water samples will indicate any major differences in accuracy and precision.

Rejection of Outliers

To determine the accuracy of each method, it was necessary to remove those extreme values which had only a small chance of validity and which would make a significant change in the accuracy measure. These values were probably caused by gross instrumental, chemical or human error. These extreme values were rejected by applying the two-tail *t*-test to all values at a 99% probability level; that is, with a 99 to 1 assurance that the data rejected were invalid and should be rejected. The data points rejected by laboratory and analyst are indicated with a capital letter, "R", after the values in Appendix 1. A greater spread of data around the true value causes rejection of fewer outliers. As the precision term in the denominator of the *t*-test increases for a method the calculated *t* value grows smaller and there are fewer extreme values rejected as outliers. An example of this is the Kjeldahl nitrogen test where no outliers were rejected because of the general imprecision of much of the data. Contrariwise, with better accuracy and precision, the *t*-test is more powerful and more outliers are rejected. An example is the total phosphorus method where one or more values were rejected for each sample tested. However, those data rejected in either case are true outliers and laboratories should carefully review procedures for the cause of inaccuracy.

Two-Sample Charts

To effectively describe the recovery values obtained for each parameter a series of two-sample charts, Figures 1 through 5, were prepared, as suggested by Youden (1). All results were plotted by parameter and by water sample type without rejection of values. Two results for each set of

similar samples (1&2), (3&4), (5&6), and (7&8) are the coordinates on the x and y axes that determined a single point for each analyst. The distribution of points (analysts) characterizes the method-results for that sample.

If random errors were responsible for the spread of results around the true values, then the data from the sample pair would be equally distributed among the four quadrants (++) (--)(+-). However, systematic error influences the data plots most and the distribution of values is not random but on a 45° slope line in the (--) and (++) quadrants, since an analyst getting a high or low value on one sample also gets a high or low value on the similar sample. This distribution of values on a 45° slope forms an elliptical pattern. Data points far removed from the elliptical cluster indicate large systematic error for one analyst compared to the other analysts. As random error decreases, data points move closer to the 45° slope. Extreme values or outliers suggest a procedure or instrument out of control. General scatter of data points away from the 45° line indicates poor precision in the method. When all data are spread far out along the 45° line, a large systematic error is indicated for the method. When precision is satisfactory but a significant bias or interference occurs the data grouping is low (--) or high (++) as in Figure 1.

DISCUSSION AND CONCLUSIONS

Ammonia Nitrogen-Distillation Method

0.21 - 0.26 mg N/liter, Ammonia Nitrogen

The manual distillation method of analyses for ammonia nitrogen showed a high and variable bias (-18 to + 5%) at ammonia nitrogen levels of 0.21 to 0.26 mg/liter. The bias was directionally negative with 3 of 4 showing >5% negative bias. There was no correlation between bias and type of water

sample (distilled and natural). The significant level of bias suggests a variable and incomplete recovery of ammonia in the distillation. This inaccuracy was compounded by standard deviations that were 32 - 56% of the levels tested, indicating further the problems in ammonia analysis at <1 mg/liter levels. At the .21 - .26 mg/liter level of ammonia nitrogen, results from natural water samples can be expected to deviate .14 - .24 mg/liter from mean values with a 95% probability.

1.71 - 1.92 mg N/liter, Ammonia Nitrogen

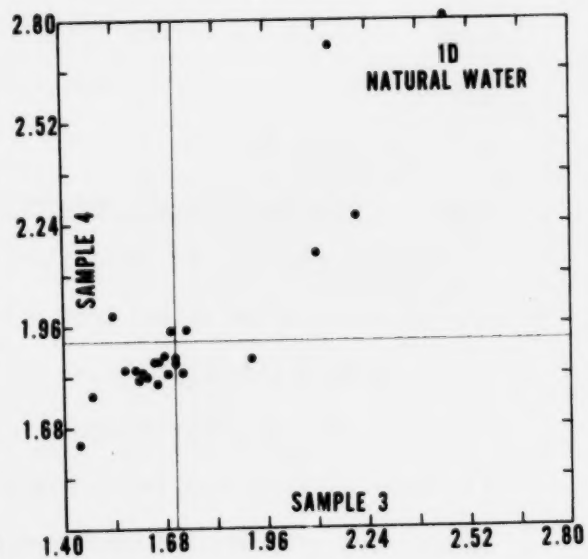
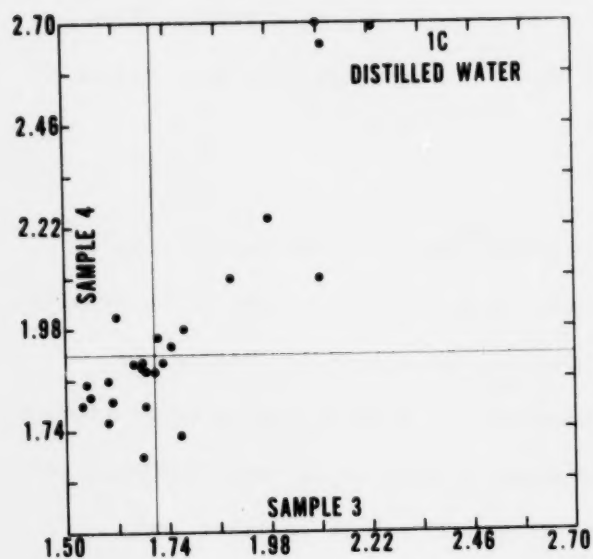
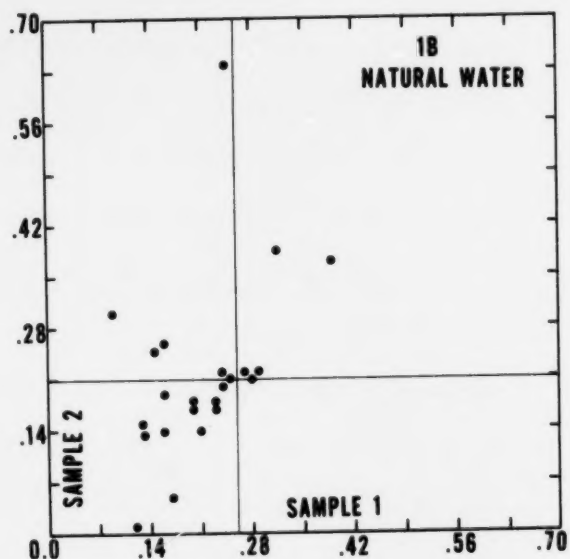
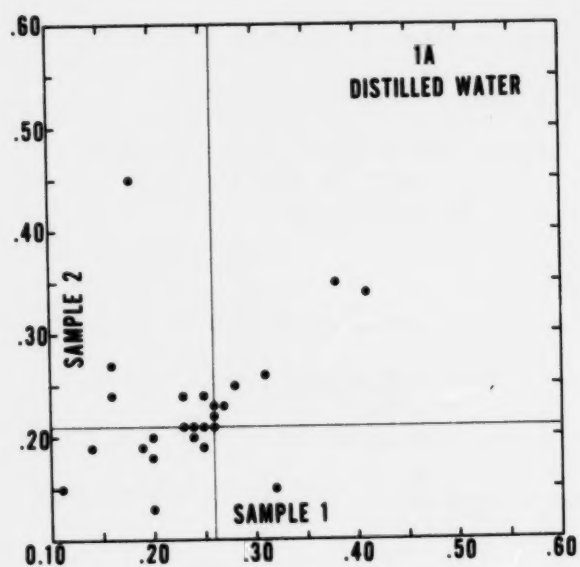
At the 2 mg/liter level, ammonia nitrogen showed good agreement between values. Standard deviations were 10 - 14% of the levels tested. Bias was reduced to 1 - 3%. Apparently, the lesser accuracy at 0.2 mg/liter was related directly to the low levels of ammonia (<1 mg/liter) rather than to the method itself.

Recoveries and precision measurements for ammonia were similar for the distilled and natural water sample indicating no interference by sample type. At the 1.7 - 1.9 mg/liter level of ammonia nitrogen results from natural water samples will deviate 0.49 - 0.56 mg/liter from mean values with a 95% probability.

Summary - Ammonia Nitrogen Analyses

In Figures 1A - 1D, most results group near the true values with a scattering of a few values some distance from the true values. The problems in the ammonia distillation are inherent in the materials, method, or technique used by a few analysts. However, the greater degree of scattering of values with the low level samples suggests that it is very difficult to obtain good accuracy and precision at this 0.21 - 0.26 mg/liter level.

FIGURE 1 A-D
TWO SAMPLE CHARTS FOR AMMONIA NITROGEN, mg N/liter



METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

13

NITROGEN - AMMONIA, AMPUL 1

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.26

N	24	RANGE	0.30035	COEF. VAR.	0.32888
TRUE VAL.	0.26	VARIANCE	0.00490	SKEWNESS	0.42922
MEAN	0.21289	STD. DEV.	0.07001	NO. OF CELLS	6
MEDIAN	0.22017	CONF LIM (95%)	0.13722		
ACCURACY	-18.11864	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.0903
0.1206
0.1300
0.1337
0.1475
0.1600
0.1602
0.1602
0.1705
0.2001
0.2003
0.2102
0.2301
0.2303
0.2401
0.2401
0.2403
0.2470
0.2507
0.2703
0.2802
0.2906
0.3150
0.3906

HISTOGRAM

CELL MID. FREQ.

0.0903	1	X
0.1503	8	XXXXXXXXX
0.2104	8	XXXXXXXXX
0.2705	5	XXXXXX
0.3305	1	X
0.3906	1	X

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METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - AMMONIA, AMPUL 2

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.21

N	24	RANGE	0.62640	COEF. VAR.	0.56118
TRUE VAL.	0.21	VARIANCE	0.01478	SKWENESS	1.68018
MEAN	0.21664	STD. DEV.	0.12157	NO. OF CELLS	6
MEDIAN	0.20022	CONF LIM. (95%)	0.23828		
ACCURACY	-5.53940	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.0106
0.0505
0.1337
0.1402
0.1402
0.1500
0.1701
0.1703
0.1801
0.1803
0.1902
0.2001
0.2003
0.2102
0.2107
0.2201
0.2203
0.2206
0.2475
0.2600
0.3003
0.3706
0.3850
0.6370 R

HISTOGRAM

CELL MID.

FREQ.

0.0106	2	XX
0.1358	9	XXXXXXXXXX
0.2611	10	XXXXXXXXXX
0.3864	2	XX
0.5117	0	
0.6369	1	X

R = REJECTED

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

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NITROGEN - AMMONIA, AMPUL 3

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 1.71

N	24	RANGE	1.01200	COEF. VAR.	0.13973
TRUE VAL.	1.71	VARIANCE	0.05970	SKEWNESS	1.48382
MEAN	1.74872	STD. DEV.	0.24435	NO. OF CELLS	6
MEDIAN	1.68530	CONF LIM. (95%)	0.47893		
ACCURACY	0.46367	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

1.4449
1.4801
1.5403
1.5701
1.6000
1.6102
1.6201
1.6302
1.6503
1.6603
1.6637
1.6803
1.6903
1.6975
1.7100
1.7102
1.7107
1.7302
1.7406
1.9206
2.1000
2.1406
2.2105
2.4570 R

HISTOGRAM

CELL MID.	FREQ.
1.4449	3 XXX
1.6473	16 XXXXXXXXXXXXXXXXXXXX
1.8497	1 X
2.0521	2 XX
2.2545	1 X
2.4569	1 X

R = REJECTED

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - AMMONIA, AMPUL 4

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 1.92

N	24	RANGE	1.17200	COEF. VAR.	0.14267
TRUE VAL.	1.92	VARIANCE	0.07783	SKEWNESS	2.16463
MEAN	1.95539	STD. DEV.	0.27898	NO. OF CELLS	6
MEDIAN	1.86200	CONF. LIM. (95%)	0.54680		
ACCURACY	-2.00814	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

1.6349

1.7701

1.8003

1.8102

1.8202

1.8301

1.8302

1.8303

1.8400

1.8401

1.8602

1.8603

1.8637

1.8701

1.8706

1.8707

1.8803

1.9475

1.9505

1.9902

2.1600

2.2604

2.7306

2.8070 R

HISTOGRAM

CELL MID.

FREQ.

1.6349

1 X

1.8694

18 XXXXXXXXXXXXXXXXXXXXX

2.1038

2 XX

2.3382

1 X

2.5725

0

2.8069

2 XX

R = REJECTED

Nitrate Nitrogen - Brucine Sulfate Method

0.16 - 0.19 mg/liter Level, Nitrate Nitrogen

The modified brucine sulfate method for nitrate nitrogen exhibited a strong negative bias at the fractional mg/liter level for 3 of 4 distilled and natural water samples. However, at these fractional mg/liter levels this negative bias is only .02 mg/liter actual difference from true value and may be acceptable. The bias and imprecision in samples containing less than 1 mg/liter of nitrate nitrogen are clearly shown in Figures 2A and 2B. Results from a natural water sample containing 0.16 - 0.19 mg/liter level of nitrate nitrogen will deviate .16 - .18 mg N/liter from mean values with a 95% probability.

1.08 - 1.24 mg/liter Level, Nitrate Nitrogen

There is a consistent positive bias at the 1 mg/liter level. With samples containing 1.08 - 1.24 mg nitrogen per liter, the standard deviations were 17 - 21% of the levels tested in natural waters. In Figures 2C and 2D, the results are tightly clumped around the true values showing improved accuracy and precision at levels above 1 mg/liter. Results from a natural water containing 1 - 1.2 mg nitrate nitrogen will deviate 0.43 - 0.49 mg N/liter from mean values with a 95% probability.

Summary - Nitrate Nitrogen Analyses

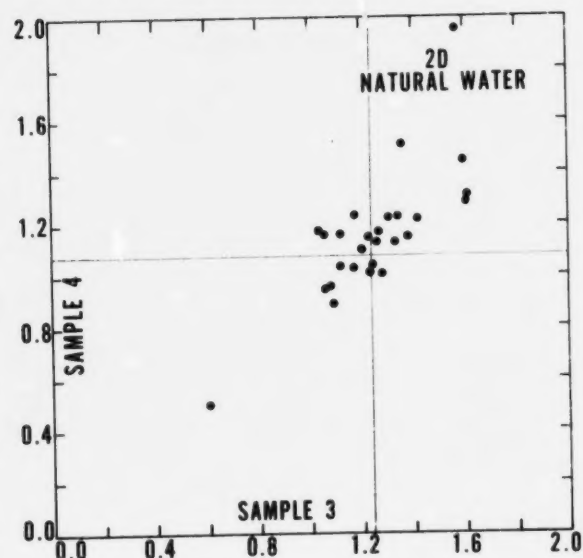
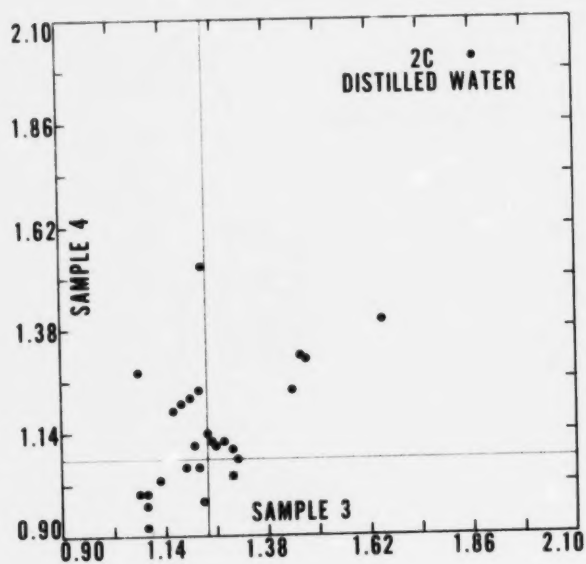
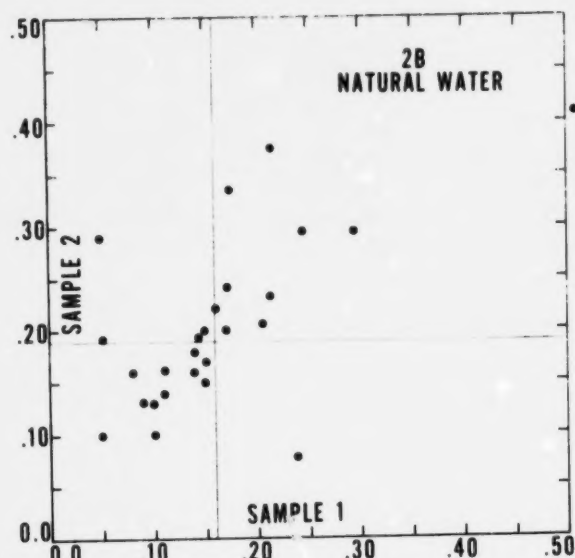
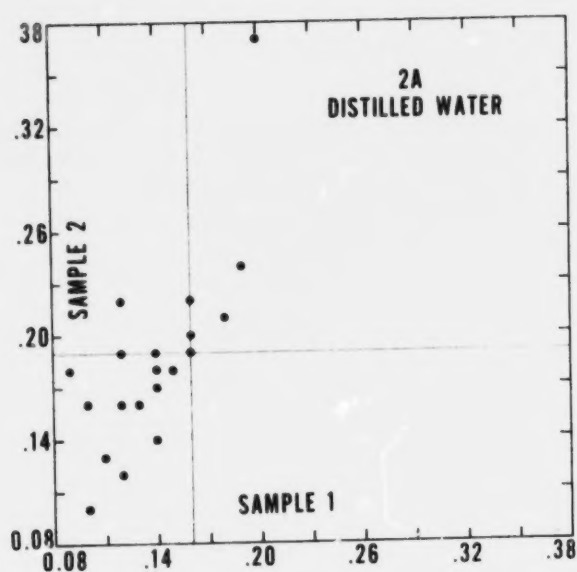
The modified brucine sulfate method for nitrate nitrogen has limited accuracy and precision at .1 - .2 mg/liter levels. The limited precision and accuracy are directly related to the level analyzed. When 1 - 2 mg N/liter is present, the brucine sulfate method shows a reduced bias and somewhat improved precision of .21 - .24 mg/liter.

The brucine method for nitrate is relatively simple and straightforward, but there may be difficulty in establishing a linear curve.

The heating step is critical and must be carefully controlled if the method is to be applied successfully. When a rack of tubes is immersed in the boiling water bath, there is a sudden temperature drop with a lag of several minutes before boiling begins again. This cooling varies with location of the tubes in the bath, and with the location of the tubes relative to location in the rack. The result is unequal color development and a corresponding loss in reproducibility.

Problems in the heating and color development can be alleviated somewhat by selection of a suitable water bath. The bath should have a tight-fitting cover, preferably with a gable configuration, it should be of sufficient depth that the tubes can be covered during the heating operation, and it should have a circulating or stirring mechanism to maintain a uniform temperature. Baths which meet these specifications are available.

FIGURE 2 A-D
TWO SAMPLE CHARTS FOR NITRATE NITROGEN, mg N/liter



METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - NITRATE, AMPL 1

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.16

N	27	RANGE	0.45829	CCEF. VAR.	0.56708
TRUE VAL.	0.16	VARIANCE	0.00852	SKEWNESS	1.94475
MEAN	0.16281	STD. LEV.	0.09232	NO. OF CELLS	6
MEDIAN	0.15015	CONF. LIM. (95%)	0.18095		
ACCURACY	-6.79206	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.0502
0.0503
0.0521
0.0801
0.0911
0.1004
0.1010
0.1102
0.1120
0.1400
0.1402
0.1438
0.1501
0.1501
0.1507
0.1610
0.1708
0.1708
0.1721
0.1756
0.2060
0.2135
0.2156
0.2385
0.2454
0.2950
0.5085 R

HISTOGRAM

CELL MID.

FREQ.

0.0502	5	XXXXX
0.1418	15	XXXXXXXXXXXXXXXXXX
0.2335	5	XXXXX
0.3251	1	X
0.4168	0	
0.5085	1	X

R = REJECTED

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

21

NITROGEN - NITRATE, AMPUL 2

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.19

N	27	RANGE	0.32999	CCEF. VAR.	0.40163
TRUE VAL.	0.19	VARIANCE	0.00683	SKENNESS	0.79922
MEAN	0.20577	STD. DEV.	0.08264	NC. OF CELLS	6
MEDIAN	0.19380	CONF. LIM. (95%)	0.16197		
ACCURACY	8.30405	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.0785
0.1003
0.1010
0.1304
0.1311
0.1402
0.1501
0.1601
0.1601
0.1620
0.1707
0.1802
0.1921
0.1938
0.2001
0.2006
0.2008
0.2060
0.2210
0.2335
0.2422
0.2902
0.2950
0.2954
0.3356
0.3756
0.4085

HISTOGRAM

CELL MID.	FREQ.	
0.0785	3	XXX
0.1445	8	XXXXXXXXXX
0.2105	10	XXXXXXXXXXXX
0.2765	3	XXX
0.3425	1	X
0.4085	2	XX

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - NITRATE, AMPUL 3

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 1.24

N	27	RANGE	1.00609	COEF. VAR.	0.17126
TRUE VAL.	1.24	VARIANCE	0.04584	SKEWNESS	-0.51751
MEAN	1.25022	STD. DEV.	0.21412	NO. OF CELLS	6
MEDIAN	1.24380	CONF. LIM. (95%)	0.41968		
ACCURACY	2.82247	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.6060
1.0356
1.0585
1.0601
1.0802
1.0911
1.1201
1.1207
1.1720
1.1756
1.2009
1.2301
1.2303
1.2438
1.2608
1.2708
1.2804
1.3035
1.3301
1.3422
1.3585
1.3810
1.4200
1.5702
1.5950
1.6054
1.6120

HISTOGRAM

CELL MID.	FREQ.
0.6060	1 X
0.8072	0
1.0084	5 XXXXX
1.2096	12 XXXXXXXXXXXXX
1.4108	5 XXXXX
1.6120	4 XXXX

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

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NITROGEN - NITRATE, AMPUL 4

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 1.08

N	27	RANGE	1.44420	CCEF. VAR.	C.21224
TRUE VAL.	1.08	VARIANCE	0.06009	SKEWNESS	C.69241
MEAN	1.15503	STD. DEV.	0.24514	NO. OF CELLS	6
MEDIAN	1.15105	CONF. LIM. (95%)	0.48047		
ACCURACY	4.11601	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.5060
0.8911
0.9500
0.9602
1.0103
1.0104
1.0320
1.0407
1.0438
1.1010
1.1301
1.1308
1.1501
1.1510
1.1585
1.1601
1.1708
1.1756
1.2200
1.2235
1.2322
1.2356
1.2854
1.3120
1.4450
1.5085
1.9502

HISTOGRAM

CELL MID.	FREQ.
0.5060	1 X
0.7948	1 X
1.0836	18 XXXXXXXXXXXXXXXXXXXX
1.3725	6 XXXXXX
1.6613	0
1.9501	1 X

Orthophosphate-Phosphorus, The Single Reagent Method

Level: .029 - .038 mg/liter, Orthophosphate-Phosphorus

The single reagent method for orthophosphate had a consistent negative bias of 5 - 13% at these low levels. In Figures 3A and 3B, though the distilled water samples showed the greatest bias, both distilled and natural water samples show low recovery so the bias is probably inherent in the method. It should be pointed out that the 5 - 13% bias at levels of 0.029 - 0.038 mg P/liter is only an absolute difference of .001 - .003 mg/liter. At the .029 - .038 mg/liter level in natural waters, orthophosphate values will deviate only .016 - .020 mg/liter from mean values with a 95% probability.

Level: .335 - .383 mg/liter, Orthophosphate-Phosphorus

At this higher level of orthophosphate, the method showed greatly improved accuracy with a negative bias of 1.2% to 2.7%. Figures 3C and 3D show almost identical pictures of this tight precision and reduced negative bias. At the 95% confidence level, the orthophosphate values will deviate .035 - .045 mg P/liter from mean values at the .335 - .383 mg P/liter levels in natural water.

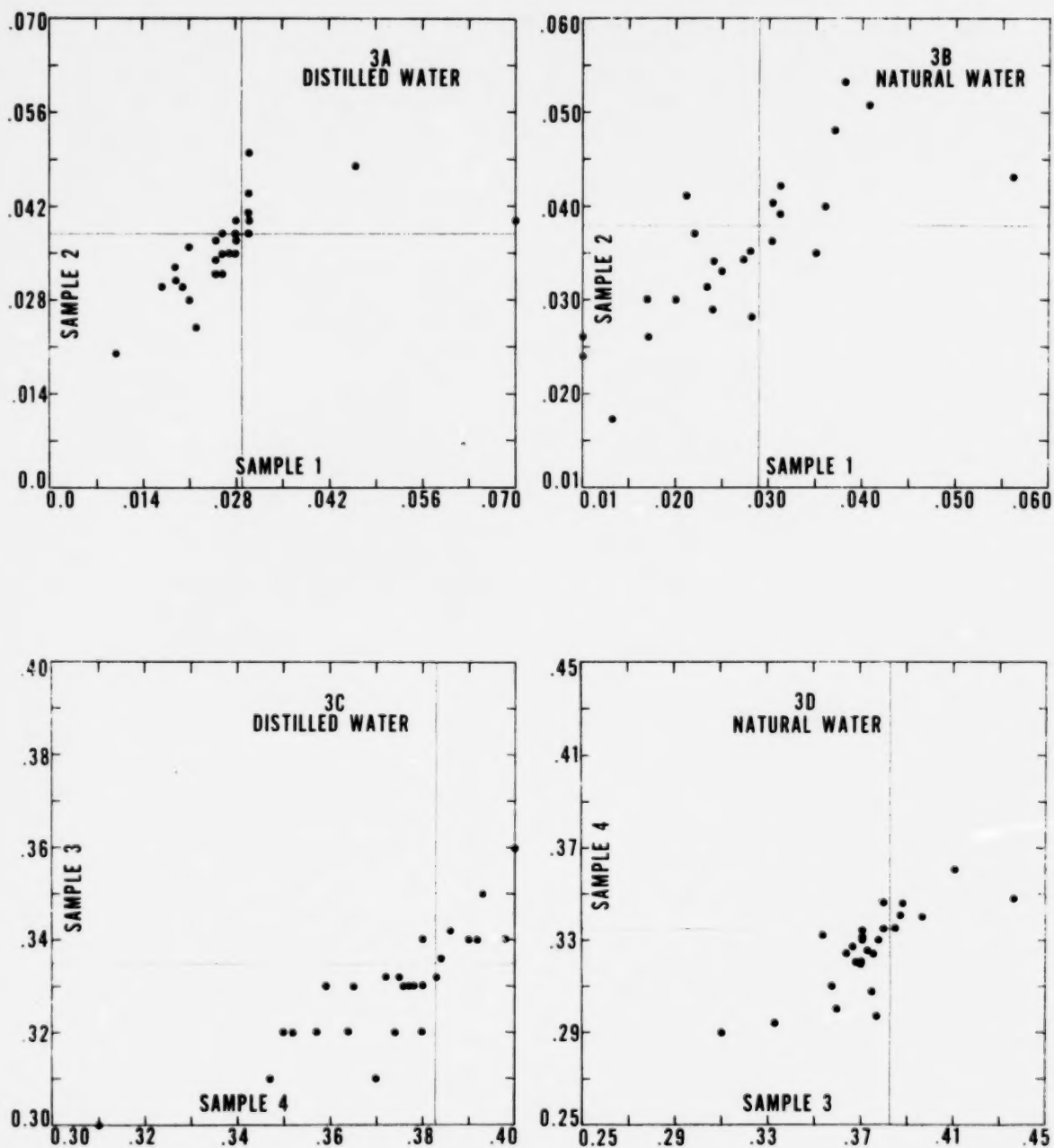
The statistical data from *Method Selection Study 1* (4) on the single reagent method for orthophosphate agree well with the data obtained here.

	Method Selection Study 1		This Study	
	Distilled Water	Natural Water	Distilled Water	Natural Water
Level added, mg/l	0.228	.228	.383, .335	.383, .335
$\bar{X}$ Recovery, mg/l	0.231	.229	.375, .331	.374, .326
Standard Deviation, mg/l	.007	.004	.019, .014	.025, .018
Accuracy, as % Bias	+2.38	+1.39	-1.58, -1.23	-1.76, -2.75

Summary - Single Reagent Method for Orthophosphate

The single reagent method for orthophosphate showed standard deviations of .008 - .023 mg P/liter and negative bias' of 1 - 6% in the 0.029 - 0.383 mg P/liter range of concentrations present in natural water samples.

FIGURE 3 A-D
TWO SAMPLE CHARTS FOR ORTHOPHOSPHATE, mg P/liter



METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

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PHOSPHATE - SCL., CRTHC, AMPUL 1

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.029

N	26	RANGE	0.04610	COEF. VAR.	0.37541
TRUE VAL.	0.029	VARIANCE	0.00010	SKEWNESS	0.50120
MEAN	0.02744	STD. DEV.	0.01030	NO. OF CELLS	6
MEDIAN	0.02771	CONF. LIM. (95%)	0.02019		
ACCURACY	-4.94894	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.0100
0.0100
0.0132
0.0170
0.0170
0.0200
0.0211
0.0221
0.0234
0.0240
0.0240
0.0250
0.0273
0.0281
0.0281
0.0303
0.0304
0.0312
0.0312
0.0351
0.0360
0.0360
0.0371
0.0382
0.0407
0.0561

HISTOGRAM

CELL MID.	FREQ.
0.0100	3 XXX
0.0192	6 XXXXXX
0.0284	10 XXXXXXXXXXXX
0.0377	6 XXXXXX
0.0469	0
0.0561	1 X

28

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

PHOSPHATE - SCL., CRTHC, AMPUL 2

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.038

N	26	RANGE	0.03596	CCEF. VAR.	0.23489
TRUE VAL.	0.038	VARIANCE	0.00006	SKEWNESS	0.11246
MEAN	0.03560	STD. DEV.	0.00836	NO. OF CELLS	6
MEDIAN	0.03510	CONF. LIM. (95%)	0.01638		
ACCURACY	-6.00358	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.0172
0.0240
0.0260
0.0260
0.0281
0.0290
0.0300
0.0300
0.0314
0.0330
0.0340
0.0343
0.0351
0.0351
0.0363
0.0371
0.0392
0.0400
0.0400
0.0404
0.0411
0.0422
0.0431
0.0481
0.0507
0.0532

HISTOGRAM

CELL MID.	FREQ.
0.0172	1 X
0.0244	3 XXX
0.0316	10 XXXXXXXXXXXX
0.0388	8 XXXXXXXXX
0.0460	2 XX
0.0532	2 XX

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

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PHOSPHATE - SOL., ORTHO, AMPL 3

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.383

N	26	RANGE	0.12621	COEF. VAR.	0.06151
TRUE VAL.	0.383	VARIANCE	0.00052	SKEWNESS	-0.06801
MEAN	0.37360	STD. DEV.	0.02298	NO. OF CELLS	6
MEDIAN	0.37230	CONF. LIM. (95%)	0.04504		
ACCURACY	-1.75849	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.3100
0.3330
0.3540
0.3580
0.3600
0.3641
0.3670
0.3683
0.3700
0.3704
0.3711
0.3711
0.3712
0.3733
0.3754
0.3760
0.3770
0.3780
0.3800
0.3802
0.3851
0.3871
0.3882
0.3971
0.4107
0.4362

HISTOGRAM

CELL MID.	FREQ.
0.3100	1 X
0.3352	1 X
0.3605	11 XXXXXXXXXXXX
0.3857	11 XXXXXXXXXXXX
0.4110	1 X
0.4362	1 X

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

PHOSPHATE - SCL., CRTHC, AMPUL 4

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.335

N	26	RANGE	0.07070	CCEF. VAR.	0.05425
TRUE VAL.	0.335	VARIANCE	0.00031	SKEWNESS	-0.35868
MEAN	0.32579	STD. DEV.	0.01767	NO. OF CELLS	6
MEDIAN	0.32855	CONF. LIM. (95%)	0.03463		
ACCURACY	-2.74782	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.2900
0.2940
0.2970
0.3000
0.3074
0.3101
0.3200
0.3203
0.3204
0.3240
0.3241
0.3253
0.3270
0.3300
0.3301
0.3311
0.3320
0.3342
0.3350
0.3351
0.3400
0.3411
0.3462
0.3462
0.3482
0.3607

HISTOGRAM

CELL MID.	FREQ.
0.2900	3 XXX
0.3041	3 XXX
0.3183	6 XXXXXX
0.3324	8 XXXXXXXX
0.3466	5 XXXXX
0.3607	1 X

Kjeldahl Nitrogen Method

The theoretical values for nitrogen can be calculated independently of the method of analysis. However, because of the extreme dependence of the Kjeldahl nitrogen test upon the type of digestion used it is difficult to obtain the same precision and accuracy as those obtained with methods for elemental analyses.

.20 - .31 mg/liter Level of Kjeldahl Nitrogen

The Kjeldahl test showed standard deviations of .15 - .22 mg N/liter with distilled water and .20 - .25 mg N/liter with natural water samples at the 0.2 - 0.3 mg/liter level. Surprisingly, there was a greater bias in the distilled water samples 24-31% positive bias, than in the natural water samples, with 5-16% positive bias.

These positive bias values are shown as a concentration of values in the (+,+) quadrants in Figures 4A and 4B. The precision at these levels was poor also, with one standard deviation being 56-59% of the added levels for distilled water samples and 75-85% of added levels for natural water samples. In Figures 4A and 4B the data extended along the 45° slope indicate the systematic error. The perpendicular spread of values away from the 45° slope indicate the serious imprecision in the method. At the 95% confidence interval, Kjeldahl nitrogen levels of 0.2 - 0.3 mg/liter will deviate $\pm$.4 - .5 mg/liter from mean values (100-200%) in natural water samples.

4.10 - 4.61 mg/liter Level of Kjeldahl Nitrogen

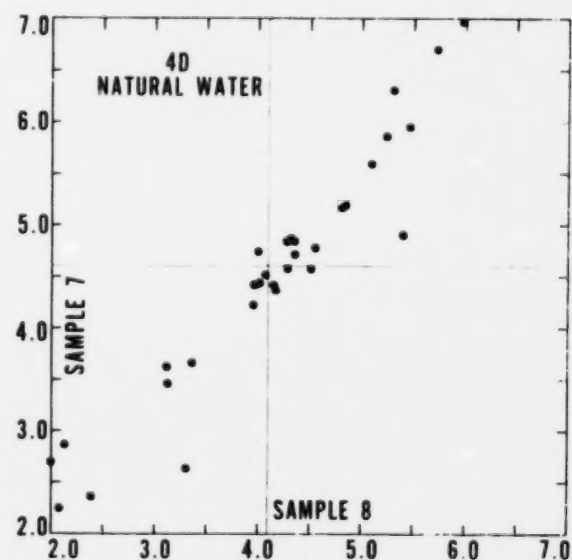
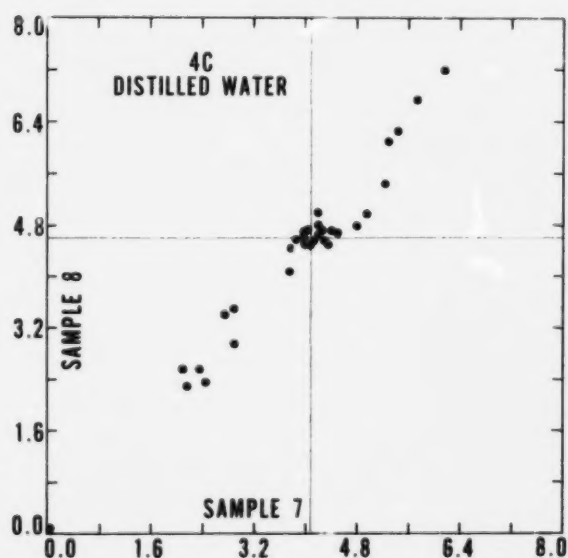
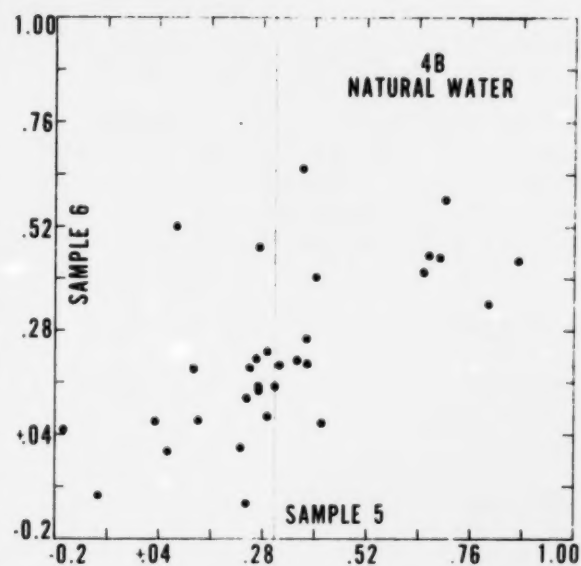
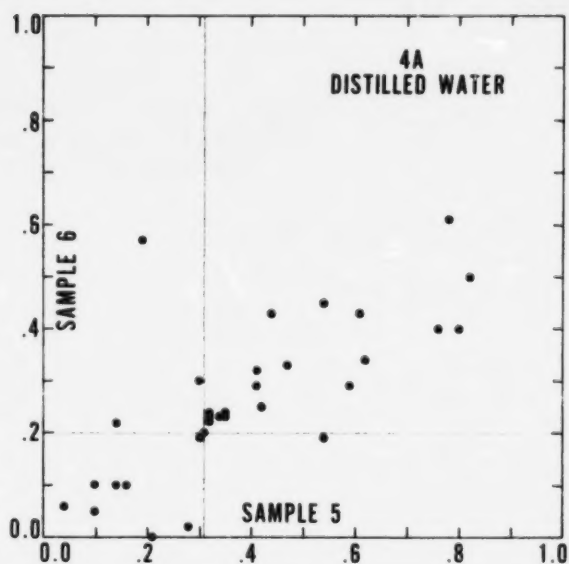
A significant improvement occurred in the Kjeldahl test at the 4 mg/liter level. Accuracy values improved to a low 1-2% positive bias for both distilled and natural waters. These very low levels of bias were offset by continuing imprecision with one standard deviation being 30-31% added values for distilled water samples and 25-26% of added values for natural water samples.

At the 95% confidence interval in natural waters, Kjeldahl nitrogen levels of 4 mg/liter deviate 2.1 to 2.3 mg N/liter from mean values. These deviations shown by the close grouping of values along extended 45° slopes in Figures 4C and 4D indicate this error is almost entirely systematic error in the method as applied in this study.

Summary - Kjeldahl Nitrogen Analyses

The Kjeldahl digestion and distillation procedures perform with very limited accuracy and precision at <1 mg/liter levels as might be expected with an operationally-defined parameter. At a level of 4 - 5 mg/liter, accuracy is greatly improved but precision is not. Major variables in the complex procedure are not completely controlled. Two quality-control factors that may give further improvement in results are greater care in protection of the samples from contamination by ammonia during analysis, and routine analysis of standard samples such as ammonium chloride and glutamic acid to check efficiency of the distillation and digestion steps.

FIGURE 4 A-D
TWO SAMPLE CHARTS FOR KJELDAHL NITROGEN, mg N/liter



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 METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
 METHOD STUDY 2, NUTRIENTS

NITROGEN - KJELD., TOT., AMPUL 5

STATISTICS, ALL DATA, ALL LABORATORIES
 MANUAL PROCEDURE
 RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = C.31

N	31	RANGE	1.05234	COEF. VAR.	0.75438
TRUE VAL.	0.31	VARIANCE	0.06081	SKEWNESS	0.36371
MEAN	0.32689	STD. DEV.	0.24660	NO. OF CELLS	6
MEDIAN	0.29180	CONF. LIM. (95%)	0.48334		
ACCURACY	5.45003	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
 ASCENDING
 ORDER

-0.1796
 -0.0994
 0.0312
 0.0612
 0.0814
 0.1215
 0.1320
 0.2301
 0.2430
 0.2439
 0.2542
 0.2670
 0.2718
 0.2728
 0.2730
 0.2918
 0.2919
 0.3118
 0.3210
 0.3617
 0.3739
 0.3817
 0.3840
 0.4050
 0.4182
 0.6539
 0.6656
 0.6908
 0.7029
 0.8027
 0.8726

HISTOGRAM

CELL MID.	FREQ.
-0.1796	2 XX
0.0307	5 XXXXX
0.2412	12 XXXXXXXXXXXXX
0.4517	6 XXXXX
0.6621	4 XXXX
0.8726	2 XX

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

35

NITROGEN - KJELD., TCT., AMPUL 6

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.20

N	31	RANGE	0.77094	CCEF. VAR.	0.85373
TRUE VAL.	0.20	VARIANCE	0.03891	SKEWNESS	0.33543
MEAN	0.23107	STD. DEV.	0.19727	NO. OF CELLS	6
MEDIAN	0.20100	CONF. LIM. (95%)	0.38665		
ACCURACY	15.53711	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

-0.1169
-0.0994
0.0012
0.0101
0.0503
0.0682
0.0708
0.0719
0.0818
0.1239
0.1428
0.1518
0.1518
0.1915
0.1942
0.2010
0.2040
0.2117
0.2170
0.2319
0.2617
0.3427
0.4050
0.4139
0.4426
0.4508
0.4556
0.4730
0.5214
0.5829
0.6539

HISTOGRAM

CELL MID. FREQ.

-0.1169	2	XX
0.0371	7	XXXXXXX
0.1913	12	XXXXXXXXXXXXX
0.3455	3	XXX
0.4997	5	XXXXX
0.6539	2	XX

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - KJELD., TCT., AMPUL 7

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 4.10

N	31	RANGE	3.97270	COEF. VAR.	0.25500
TRUE VAL.	4.10	VARIANCE	1.11570	SKEWNESS	-0.46739
MEAN	4.14219	STD. DEV.	1.05626	NO. OF CELLS	6
MEDIAN	4.28180	CONF. LIM. (95%)	2.07027		
ACCURACY	1.02903	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

2.0015
2.0809
2.1312
2.3920
3.1219
3.1304
3.3049
3.3670
3.9614
3.9716
4.0056
4.0209
4.0739
4.1617
4.1682
4.2818
4.2827
4.3218
4.3418
4.3539
4.5139
4.5601
4.8108
4.8430
5.0930
5.2427
5.3039
5.4050
5.4626
5.7229
5.9742

HISTOGRAM

CELL MID.

FREQ.

2.0015	4	XXXX
2.7960	2	XX
3.5905	4	XXXX
4.3851	12	XXXXXXXXXXXXXX
5.1796	7	XXXXXXX
5.9741	2	XX

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

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NITROGEN - KJELC., TCT., AMPL 8

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 4.61

N	31	RANGE	4.71329	CCEF. VAR.	0.26282
TRUE VAL.	4.61	VARIANCE	1.41948	SKWNESS	-0.10507
MEAN	4.53315	STD. DEV.	1.19142	NO. OF CELLS	6
MEDIAN	4.57395	CONF. LIM. (95%)	2.33518		
ACCURACY	-1.66690	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

2.2509
2.3619
2.6349
2.7015
2.8712
3.4605
3.6219
3.6670
4.2214
4.3682
4.4117
4.4216
4.4409
4.5139
4.5727
4.5739
4.7139
4.7456
4.7800
4.8418
4.8418
4.8618
4.9050
5.1708
5.2030
5.5930
5.8627
5.9526
6.3039
6.6929
6.9642

HISTOGRAM

CELL MID.	FREQ.
2.2509	4 XXXX
3.1935	3 XXX
4.1362	9 XXXXXXXXXXXX
5.0788	9 XXXXXXXXXXXX
6.0215	4 XXXX
6.9641	2 XX

Total Phosphorus - The Persulfate Digestion and Single Reagent Method

0.110 - .132 mg/liter Level of Total Phosphorus

At this low level, the total phosphorus was recovered with accuracy of +.6% to -1% bias in distilled water and 3-12% positive bias in natural waters. This positive bias in natural water (Figure 5B) is in contrast to the 5-13% negative bias observed for orthophosphate. Although 12% is a relatively high bias, the level is only 0.01 - 0.026 mg/liter which is barely above the minimum detectable level. At this fractional mg/liter level, the total phosphorus method operated with limited precision, showing a 95% chance for variability of $\pm 0.06 - .10$ mg/liter from mean values in natural water samples containing .12 - .13 mg P/liter.

The precision was similar for distilled and natural water samples so the variation relates to the method not to the sample type. It is also similar to the precision found for orthophosphate in samples 1 and 2. The apparently greater spread of values shown in Figure 5A over those shown in Figure 5B is the result of 2.5 scale expansion in 5A over 5B. The accuracy of the test is clearly shown in the tight centering of values around the true value intersect.

0.772 - .882 mg/liter Level of Total Phosphorus

At these higher fractional levels, the total phosphorus analysis showed -2% to +3% bias in distilled and natural water samples. Figures 5C and 5D show this tight grouping of values around the true value intersect. At the 95% confidence interval, total phosphorus mean values of .81 and .89 mg/liter deviated ± 0.25 mg P/liter in natural waters.

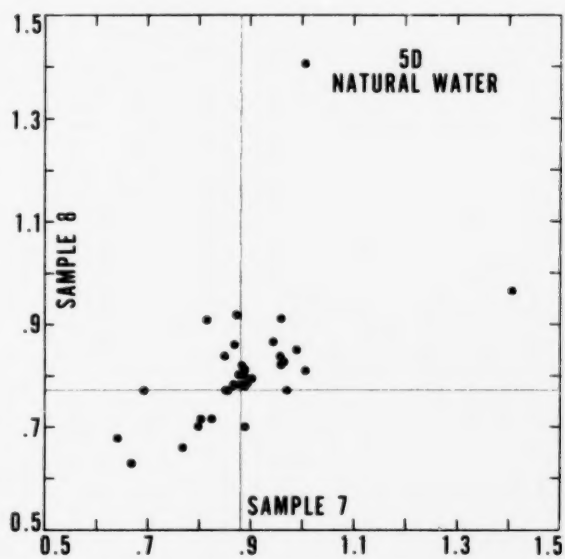
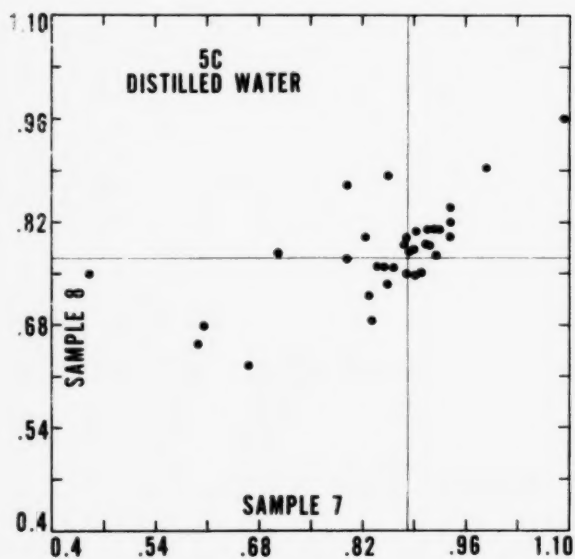
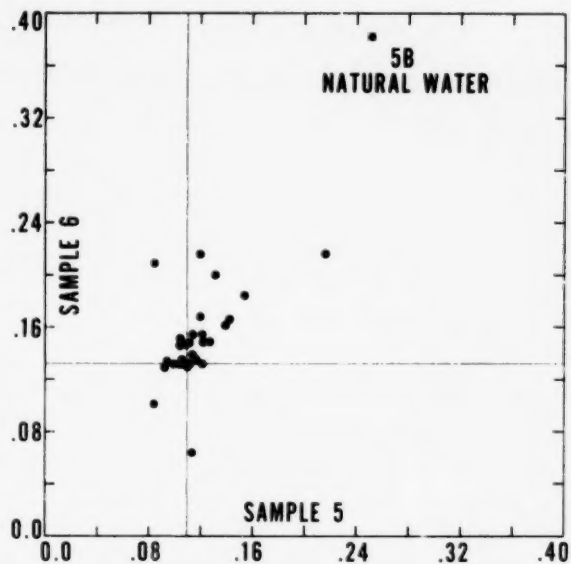
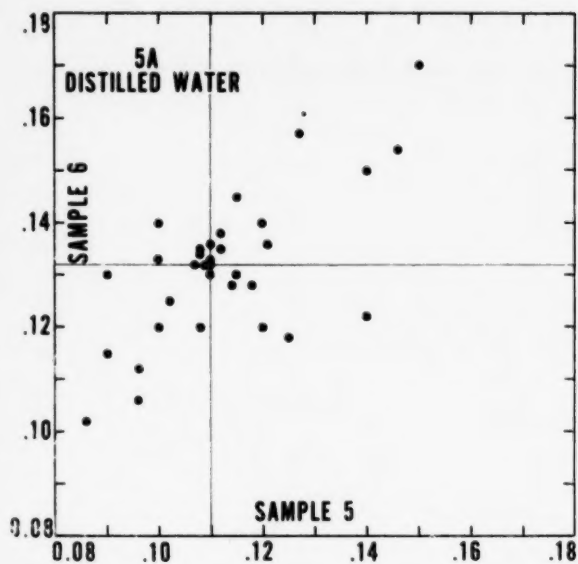
Summary - Total Phosphorus Analyses

The accuracy and precision of the single reagent method for orthophosphate are reflected in the tight grouping and limited scatter of most laboratory values around the true and mean values for both the 0.1 and 0.8

mg P/liter samples. This grouping also emphasizes the extreme values obtained by a few laboratories.

The precision was lessened apparently by the additional variable, the persulfate digestion step. Perhaps this also changed the negative bias of the orthophosphate test to a positive bias in the total phosphorus test.

FIGURE 5 A-D
TWO SAMPLE CHARTS FOR TOTAL PHOSPHORUS, mg P/liter



METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

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PHOSPHORUS - TCTAL, AMPUL 5

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.110

N	33	RANGE	0.16691	CCEF. VAR.	0.27410
TRUE VAL.	0.110	VARIANCE	0.00109	SKEWNESS	2.59996
MEAN	0.12068	STD. DEV.	0.03308	NO. OF CELLS	6
MEDIAN	0.11318	CONF. LIM. (95%)	0.06484		
ACCURACY	3.09078	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.0841
0.0848
0.0921
0.0943
0.0992
0.1011
0.1050
0.1051
0.1053
0.1061
0.1063
0.1091
0.1101
0.1111
0.1111
0.1111
0.1111
0.1131
0.1141
0.1142
0.1162
0.1198
0.1201
0.1210
0.1212
0.1214
0.1222
0.1272
0.1321
0.1390
0.1426
0.1540
0.2162
0.2510

HISTOGRAM

CELL MID. FREQ.

0.0841	5	XXXXXX
0.1175	23	XXXXXXXXXXXXXXXXXXXXXXXXXXXX
0.1509	3	XXX
0.1842	0	
0.2176	1	X
0.2510	1	X

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

PHOSPHORUS - TOTAL, AMPUL 6

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.132

N	33	RANGE	0.31787	COEF. VAR.	0.33055
TRUE VAL.	0.132	VARIANCE	0.00262	SKEWNESS	2.68853
MEAN	0.15492	STD. DEV.	0.05121	NO. OF CELLS	6
MEDIAN	0.14502	CONF. LIM. (95%)	0.100 37		
ACCURACY	11.99398	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.0641

0.1011

0.1291

0.1291

0.1311

0.1311

0.1311

0.1311

0.1312

0.1312

0.1314

0.1333

0.1341

0.1343

0.1352

0.1382

0.1450

0.1461

0.1471

0.1482

0.1482

0.1503

0.1540

0.1541

0.1610

0.1656

0.1678

0.1840

0.2001

0.2088

0.2161

0.2162

0.3820

HISTOGRAM

CELL MID.

FREQ.

0.0641

1 X

0.1277

23 XXXXXXXXXXXXXXXXXXXXXXXXXX

0.1913

8 XXXXXXXXX

0.2549

0

0.3184

0

0.3820

1 X

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

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PHOSPHORUS - TOTAL, AMPUL 7

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.882

N	33	RANGE	0.76499	COEF. VAR.	0.14437
TRUE VAL.	0.882	VARIANCE	0.01651	SKEWNESS	1.59664
MEAN	0.89004	STD. DEV.	0.12850	NO. OF CELLS	6
MEDIAN	0.88409	CONF LIM. (95%)	0.25186		
ACCURACY	0.91260	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.6421
0.6690
0.6921
0.7683
0.8000
0.8051
0.8160
0.8273
0.8503
0.8530
0.8561
0.8702
0.8708
0.8742
0.8780
0.8811
0.8840
0.8902
0.8902
0.8911
0.8941
0.8951
0.9041
0.9446
0.9581
0.9600
0.9614
0.9640
0.9711
0.9902
1.0048
1.0062
1.4071

HISTOGRAM

CELL MID.	FREQ.
0.6421	3 XXX
0.7951	10 XXXXXXXXXXXX
0.9481	19 XXXXXXXXXXXXXXXXXXXX
1.1011	0
1.2541	0
1.4071	1 X

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

PHOSPHORUS - TOTAL, AMPUL 8

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM NATURAL WATER

INCREMENT = 0.772

N	33	RANGE	0.77719	COEF. VAR.	0.16041
TRUE VAL.	0.772	VARIANCE	0.01702	SKEWNESS	2.82262
MEAN	0.81341	STD. DEV.	0.13048	NO. OF CELLS	6
MEDIAN	0.79418	CONF. LIM. (95%)	0.25574		
ACCURACY	2.96449	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.6290
0.6603
0.6781
0.7000
0.7002
0.7151
0.7153
0.7710
0.7711
0.7711
0.7711
0.7808
0.7811
0.7811
0.7841
0.7931
0.7941
0.7990
0.8098
0.8102
0.8200
0.8200
0.8260
0.8361
0.8373
0.8502
0.8602
0.8646
0.9090
0.9114
0.9182
0.9661
1.4062

HISTOGRAM

CELL MID.

FREQ.

0.6290	5	XXXXX
0.7844	22	XXXXXXXXXXXXXXXXXXXXXXX
0.9399	5	XXXXX
1.0953	0	
1.2507	0	
1.4062	1	X

Characterization of Natural Waters

The following are examples of the natural waters tested in this study:

Water Source	Spec. Cond.	pH	TDS	Total Hardness	Acidity Alkalinity	Cl	SO ₄
Mary's River	139	7.2	--	34	38	12	<10
Missouri River	500-1000	6.5-8.5	500-1000	150-1000	100-250	<50	100-500
Raritan Bay	19000	7.6	22,500	>500	890	10,200	>500
Ohio River	390	6.9	259	147	30	25	100
Raritan Bay	36000	7.8	25,700	5400	82	14000	>500
Pacific Ocean	14,800	8.1	--	5700	110	--	2450
Chena River	213	7.4	145	100	86	1.8	26
Stonelick Creek	306	7.9	216	151	105	10	31
Indiana Harbor Canal	500-1000	6.5-8.5	100-500	50-150	50-150	<50	50-150
San Joaquin River	100-500	6.5-8.5	100-500	<50	<50	<50	<50
Colorado River	1300	8.2	850	340	213	136	355
Deschutes River	118	7.85	103	51	40	8.5	--
Detroit River	300	8.2	--	--	76	40	<50
Lake Ontario	100-	6.5-8.5	100-500	50-150	50-100	<50	<50
Nashua River	180	6.8	37	84	28	20	20
Shagawa Lake	100-500	6.5-8.5	100-500	<50	50-100	<50	<50
Rock Creek	1440	6.3	1570	228	670	5	20

Interferences from Natural Waters

Throughout this study, laboratories reported extreme values in recovery of increments from natural waters such as estuaries, fresh waters high in dissolved solids, and waters heavily polluted with industrial wastes, any of which might interfere with analyses. However, an examination of the recoveries of increments from distilled water samples from these laboratories showed about the same pattern of extreme values. This suggests that the imprecision of their data was largely related to technique, and that the only effect of the natural water samples was to exaggerate their difficulties. Based on this study, the WQO methods of analyses are applicable to varying types of fresh and saline waters.

REFERENCES

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3. Larsen, K. E. 1969. The Summarization of Data. *J. Qual. Technol.*, Vol. 1, No. 1, 1968.
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APPENDIX 1

Tabulation of Data

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - AMMONIA

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE

RECOVERY OF INCREMENT FROM DISTILLED WATER, MG/L

LAB NO.	ANALYST NO.	INCREMENT, MG/L	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4
101	1	0.26	0.26	0.21	1.71	1.92

LAB NO.	ANALYST NO.
101	1
101	2
102	1
106	2
107	1
107	4
110	1
110	2
110	3
110	4
110	5
112	1
113	1
113	3
113	4
113	5
114	1
114	2
115	2
116	3
121	1
123	1
123	2
123	3
125	3
126	2
126	3
127	2
134	1

0.19	0.19	1.75	1.94
0.20	0.20	1.71	1.88
0.38	0.35	1.73	1.90
0.27	0.23	1.89	2.10
0.25	0.21	1.55	1.85
0.26	0.21	1.60	1.86
0.11	0.15	1.54	1.80
0.14	0.19	1.98	2.24
0.18	0.45R	1.72	1.96
0.16	0.27	1.62	2.01
0.25	0.19	1.68	1.68
0.24	0.21	1.68	1.90
0.24	0.20	1.69	1.80
0.20	0.18	1.56	1.82
0.23	0.21	1.61	1.81
0.41	0.34	2.10	2.10
0.28	0.25	1.69	1.88
0.26	0.23	1.68	1.89
0.23	0.24	1.66	1.90
0.26	0.22	1.77	1.73
0.31	0.26	1.78	1.98
0.25	0.24	1.60	1.76
0.20	0.13	2.11	2.65R
0.32	0.15	2.23R	2.69R
0.16	0.24	1.72	1.96
0.51R	0.44R	2.10	2.70R

R = REJECTED

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - AMMONIA

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE

COMPUTED RECOVERY OF INCREMENT FROM NATURAL WATER, MG/L

LAB NO.	ANALYST NO.	INCREMENT, MG/L	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4
101	1	0.26	0.26	0.21	1.71	1.92

LAB NO.	ANALYST NO.
101	1
101	2
102	1
107	1
107	4
110	1
110	2
110	3
110	4
110	5
112	1
113	1
113	3
113	4
114	1
115	2
116	3
121	1
123	1
123	2
125	3
126	2
126	3
127	2
134	1

0.2102	0.1402	1.7102	1.8602
0.1602	0.1402	1.7302	1.8302
0.3150	0.3850	1.4449	1.6349
0.2401	0.2201	1.4801	1.7701
0.2401	0.2001	1.6201	1.8301
0.1300	0.1500	1.6000	1.8400
0.1600	0.2600	2.1000	2.1600
0.2470	0.6370R	2.4570R	2.8070R
0.0903	0.3003	1.5403	1.9902
-0.7150R	-0.7650R	0.8150R	0.8150R
0.2301	0.1801	1.7100	1.8701
0.2303	0.1703	1.6603	1.8003
0.2001	0.1701	1.5701	1.8401
0.2003	0.1803	1.6803	1.8803
0.1337	0.1337	1.6637	1.8637
0.2507	0.2107	1.7107	1.8707
0.2403	0.2003	1.6503	1.8603
0.1602	0.1902	1.6302	1.8202
0.2703	0.2203	1.6903	1.8303
0.2906	0.2206	1.7406	1.9505
0.2802	0.2102	1.6102	1.8102
0.1206	0.0106	2.1406	2.7306R
0.1705	0.0505	2.2105	2.2604
0.1475	0.2475	1.6975	1.9475
0.3906	0.3706	1.9206	1.8706

R = REJECTED

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - NITRATE

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE

COMPUTED RECOVERY OF INCREMENT FROM NATURAL WATER, MG/L

INCREMENT, MG/L	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	LAB NO.	ANALYST NO.
0.16	0.16	0.19	1.24	1.08	101	1
0.16	0.0785	0.0785	1.0585	1.1585	101	2
0.16	0.5085R	0.4085R	1.3585	1.5085	102	2
0.16	0.1610	0.2210	1.3810	1.1510	107	4
0.16	0.1708	0.2008	1.2708	1.1708	107	5
0.16	0.1708	0.2008	1.2608	1.1308	107	1
0.16	0.1756	0.3356	1.1756	1.2356	110	2
0.16	0.2156	0.3756	1.0356	1.1756	110	3
0.16	0.0502	0.2902	1.5702	1.9502R	110	4
0.16	0.2454	0.2954	1.6054	1.2854	110	5
0.16	0.2060	0.2060	0.6060R	0.5060	112	1
0.16	0.1400	0.1601	1.0601	0.9500	112	3
0.16	0.2135	0.2335	1.3035	1.2235	113	1
0.16	0.0911	0.1311	1.0911	0.8911	113	3
0.16	0.2950	0.2950	1.5950	1.4450	114	4
0.16	0.1010	0.1010	1.2009	1.1010	115	1
0.16	0.1004	0.1304	1.2804	1.0104	115	2
0.16	0.1402	0.1802	1.3301	1.1301	116	4
0.16	0.1120	0.1620	1.1720	1.0320	121	1
0.16	0.1507	0.1707	1.1207	1.0407	121	1
0.16	0.1501	0.2001	1.2301	1.1501	122	1
0.16	0.0521	0.1921	1.6120	1.3120	123	2
0.16	0.1721	0.2422	1.3422	1.2322	123	3
0.16	0.1102	0.1402	1.0802	0.9602	125	2
0.16	0.0801	0.1601	1.1201	1.1601	126	3
0.16	0.1501	0.1501	1.4200	1.2200	126	3
0.16	0.1438	0.1938	1.2438	1.0438	127	2
0.16	0.0503	0.1003	1.2303	1.0103	134	1

R = REJECTED

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - NITRATE

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE

RECOVERY OF INCREMENT FROM DISTILLED WATER, MG/L

INCREMENT, MG/L	AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	LAB NO.	ANALYST NO.
0.16	0.16	0.19	1.24	1.08	101	1
0.16	0.00	0.00R	1.10	0.92	101	2
0.16	0.14	0.14	1.08	1.28	102	2
0.16	0.13	0.16	1.28	1.12	107	4
0.16	0.11	0.13	1.21	1.11	107	5
0.16	0.16	0.19	1.24	1.14	107	1
0.16	0.16	0.19	1.30	1.10	110	2
0.16	0.09	0.18	1.22	1.22	110	3
0.16	0.09R	0.18	1.24	1.24	110	4
0.16	0.12	0.19	1.87R	2.01R	110	5
0.16	0.14	0.19	1.47	1.31	112	1
0.16	0.10	0.10	1.10	1.00	112	3
0.16	0.14	0.17	1.10	0.97	113	1
0.16	0.14	0.18	1.26	1.11	113	3
0.16	0.12	0.16	1.13	1.03	113	4
0.16	0.19	0.24	1.65	1.40	114	1
0.16	0.10	0.10	1.30	1.10	115	2
0.16	0.16	0.20	1.31	1.08	115	4
0.16	0.15	0.18	1.19	1.06	116	1
0.16	0.12	0.12	1.23	0.98	121	1
0.16	0.20	0.20	1.21	1.11	122	1
0.16	0.15	0.18	1.18	1.21	123	2
0.16	0.20	0.37R	1.23	1.53	123	3
0.16	0.12	0.22	1.44	1.24	125	2
0.16	0.14	0.17	1.08	1.00	126	3
0.16	0.10	0.16	1.19	1.19	126	3
0.16	0.16	0.22	1.46	1.32	127	2
0.16	0.16	0.20	1.22	1.06	127	2
0.16	0.18	0.21	1.25	1.12	128	1
0.16	0.12	0.12	1.30	1.04	134	1

R = REJECTED

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

ORTHO PHOSPHATE

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE

COMPUTED RECOVERY OF INCREMENT FROM NATURAL WATER, MG/L

RECOVERY OF INCREMENT FROM DISTILLED WATER, MG/L

LAB NO.	ANALYST NO.	INCREMENT, MG/L				LAB NO.	ANALYST NO.	INCREMENT, MG/L			
		AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4			AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4
101	1	0.030	0.038	0.383	0.335	101	1	0.0273	0.0343	0.3683	0.3203
101	2	0.030	0.038	0.383	0.332	101	2	0.0303	0.0363	0.3733	0.3253
102	3	0.020	0.030	0.380	0.340	102	3	0.0211	0.0411	0.3711	0.3311
106	2	0.028	0.037	0.365	0.330	107	1	0.0360	0.0400	0.3800	0.3350
107	1	0.028	0.035	0.375	0.332	107	5	0.0360	0.0400	0.3780	0.3300
107	5	0.027	0.035	0.372	0.332	110	1	0.0100	0.0260	0.3600	0.3000
110	1	0.010	0.020R	0.350	0.320	110	2	0.0100	0.0240	0.3100R	0.2900R
110	2	0.010	0.020R	0.352	0.320	110	3	0.0281	0.0281	0.3641	0.3241
110	3	0.021	0.028	0.357	0.320	110	4	0.0200	0.0300	0.3540	0.3320
110	4	0.022	0.024	0.359	0.330	110	5	0.0170	0.0300	0.3770	0.2970
110	5	0.017	0.030	0.380	0.320	112	1	0.0240	0.0290	0.3700	0.3200
112	1	0.021	0.036	0.378	0.330	113	1	0.0312	0.0392	0.3882	0.3462
113	1	0.070R	0.040	0.393	0.350	113	3	0.0371	0.0481	0.3971	0.3400
113	3	0.030	0.044	0.398	0.340	113	4	0.0312	0.0422	0.3802	0.3462
113	4	0.028	0.038	0.384	0.336	114	1	0.0407	0.0507	0.4107	0.3607
114	1	0.030	0.040	0.400	0.360	115	1	0.0234	0.0314	0.3754	0.3074
115	1	0.019	0.033	0.374	0.320	115	2	0.0304	0.0404	0.3704	0.3204
115	2	0.030	0.050	0.380	0.330	116	1	0.0221	0.0371	0.3871	0.3411
116	1	0.026	0.035	0.386	0.342	121	1	0.0132	0.0172	0.3712	0.3342
121	1	0.026	0.032	0.376	0.330	122	1	0.0382	0.0532	0.4362	0.3482
122	1	0.046	0.048	0.400	0.360	123	1	0.0240	0.0340	0.3760	0.3240
123	1	0.028	0.040	0.392	0.340	123	2	0.0250	0.0330	0.3670	0.3270
123	2	0.026	0.038	0.377	0.330	125	4	0.0170	0.0260	0.3330	0.2940
125	4	0.025	0.037	0.347	0.310	126	3	0.0281	0.0351	0.3580	0.3101
126	2	0.030	0.041	0.390	0.340	127	2	0.0351	0.0351	0.3851	0.3351
126	3	0.025	0.034	0.364	0.320	134	1	0.0561R	0.0431	0.3711	0.3301
127	2	0.028	0.040	0.390	0.340						
128	2	0.025	0.032	0.310R	0.300R						
134	1	0.019	0.031	0.370	0.310						

R = REJECTED

R = REJECTED

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

KJELDAHL NITROGEN

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE

RECOVERY OF INCREMENT FROM DISTILLED WATER, MG/L

LAB NO.	ANALYST NO.	AMPUL 5	AMPUL 6	AMPUL 7	AMPUL 8	INCREMENT, MG/L
101	2	0.59	0.29	4.20	4.66	4.61
102	1	0.82	0.50	4.00	4.70	4.61
106	1	0.32	0.24	4.22	4.80	4.61
106	2	0.32	0.22	4.26	4.72	4.61
106	3	0.35	0.24	4.30	4.57	4.61
107	1	0.30	0.19	4.12	4.55	4.61
107	3	0.34	0.23	4.00	4.50	4.61
110	1	0.76	0.40	5.44	6.26	4.61
110	2	0.80	0.40	5.30	6.10	4.61
110	3	0.41	0.29	2.90	3.50	4.61
110	4	0.78	0.61 R	5.74	6.74	4.61
110	5	0.10	0.10	2.56	2.56	4.61
110	6	0.14	0.22	2.16	2.29	4.61
112	1 FW	0.16	0.10	2.45	2.35	4.61
112	1 EW	0.14	0.10	2.36	2.56	4.61
113	1	0.16	0.10	3.84	4.58	4.61
113	3	0.19	0.57	3.76	4.08	4.61
113	4	0.54	0.45	4.42	4.72	4.61
114	1	0.44	0.43	4.80	4.80	4.61
115	2	0.10	0.05	2.75	3.40	4.61
116	3	0.31	0.20	4.08	4.50	4.61
117	1	0.30	0.30	3.78	4.44	4.61
120	1	0.04	0.06	0.03 R	0.10 R	4.61
121	1	0.32	0.23	4.35	4.50	4.61
123	1	0.47	0.33	4.02	4.71	4.61
123	2	0.41	0.32	4.95	4.98	4.61
125	1	0.54	0.19	4.20	5.00	4.61
126	2	0.42	0.25	6.16	7.19	4.61
126	3	0.35	0.23	5.23	5.45	4.61
127	2	0.28	0.02	4.06	4.72	4.61
129	3	--	--	4.01	4.68	4.61
130	1	0.21	0.00	4.47	4.68	4.61
134	1	0.61	0.43	2.90	2.95	4.61

FW = FRESH WATER

EW = ESTUARINE WATER

R = REJECTED

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

KJELDAHL NITROGEN

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE

COMPUTED RECOVERY OF INCREMENT FROM NATURAL WATER, MG/L

LAB NO.	ANALYST NO.	INCREMENT, MG/L	AMPUL 5	AMPUL 6	AMPUL 7	AMPUL 8
101	1	0.6539	0.4139	0.4139	4.3539	4.7139
101	2	0.3739	0.6539	0.6539	4.0739	4.5139
102	1	0.4182	0.0682	0.0682	4.1682	4.3682
106	1	0.3118	0.1518	0.1518	4.3418	4.8418
106	2	0.2718	0.1518	0.1518	4.3218	4.8618
106	3	0.2918	0.0818	0.0818	4.2818	4.8418
107	1	0.3817	0.2617	0.2617	4.1617	4.4117
107	3	0.3617	0.2117	0.2117	3.9716	4.4216
110	1	0.8726	0.4426	0.4426	5.4626	5.9526
110	2	0.8027	0.3427	0.3427	5.2427	5.8627
110	3	0.2919	0.2319	0.2319	3.1219	3.6219
110	4	0.7029	0.5829	0.5829	5.7229	6.6929
110	5	0.1215	0.1915	0.1915	2.0015	2.7015
110	6	0.0612	0.0012	0.0012	2.1312	2.8712
112	1 FW	0.1320	0.0719	0.0719	2.3920	2.3619
112	1 EW	0.0312	0.0708	0.0708	2.0809	2.2509
113	1	-0.1796	0.0503	0.0503	3.3049	2.6349
113	3	0.0814	0.5214	0.5214	3.9614	4.2214
113	4	0.2670	0.2170	0.2170	3.3670	3.6670
114	1	0.4050	0.4050	0.4050	5.4050	4.9050
115	2	-0.0994	-0.0994	-0.0994	3.1304	3.4605
116	3	0.3210	0.2010	0.2010	4.0209	4.4409
117	1	0.6656	0.4556	0.4556	4.0056	4.7456
120	1	0.4700	-0.0001	-0.0001	0.1223	0.0009
121	1	0.2728	0.1428	0.1428	4.5727	4.5727
123	2	0.2439	0.1239	0.1239	4.5139	4.5739
125	1	0.2430	-0.1169	-0.1169	4.8430	5.2030
126	2	0.2542	0.1942	0.1942	5.9742	6.9642
126	3	0.2730	0.4730	0.4730	5.0930	5.5930
127	2	0.6908	0.4508	0.4508	4.8108	5.1708
130	1	0.2301	0.0101	0.0101	4.5601	4.7800
134	1	0.3840	0.2040	0.2040	5.3039	6.3039

FW = FRESH WATER

EW = ESTUARINE WATER

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

TOTAL PHOSPHORUS

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE

RECOVERY OF INCREMENT FROM DISTILLED WATER, MG/L

LAB NO.	ANALYST NO.	INCREMENT, MG/L	AMPUL 5	AMPUL 6	AMPUL 7	AMPUL 8
101	1	0.108	0.134	0.925	0.810	
101	2	0.108	0.135	0.908	0.790	
102	3	0.140	0.150	0.900	0.750	
106	1	0.090	0.130	0.850	0.760	
106	2	0.090	0.115	0.840	0.760	
106	3	0.100	0.120	0.840	0.760	
107	3	0.118	0.128	0.884	0.780	
107	4	0.114	0.128	0.876	0.790	
110	1	0.110	0.130	0.940	0.820	
110	2	0.100	0.140	0.940	0.800	
110	3	0.086	0.102	0.606	0.678	
110	4	0.096	0.112	0.706	0.778	
110	5	0.100	0.133	0.829	0.720	
110	6	0.110	0.136	0.855	0.735	
112	1FW	0.109	0.132	0.920	0.775	
112	1EW	0.115	0.145	0.890	0.783	
113	1	0.121	0.136	0.909	0.810	
113	3	0.125	0.118	0.855	0.883	
113	4	0.112	0.135	0.825	0.800	
114	1	0.120	0.140	0.920	0.810	
115	1	0.110	0.133	0.988	0.894	
116	1	0.112	0.138	0.893	0.807	
117	1	0.110	0.132	0.452 R	0.750	
120	1	0.146	0.154	0.800	0.870	
121	1	0.108	0.120	0.892	0.747	
122	1	0.120	0.120	0.800	0.770	
123	1	0.118	0.128	0.940	0.840	
123	2	0.107	0.132	0.911	0.788	
125	4	0.102	0.125	0.833	0.685	
126	2	0.109	0.132	0.863	0.758	
126	3	0.127	0.157	1.094	0.961 R	
127	2	0.115	0.130	0.880	0.799	
128	2	0.140	0.122	0.880	0.750	
129	3	--	0.923	0.923	--	
130	1	0.150 R	0.170 R	0.665	0.625	
134	1	0.096	0.106	0.597	0.654	

FW = FRESH WATER
EW = ESTUARINE WATER

R = REJECTED

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

TOTAL PHOSPHORUS

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE

COMPUTED RECOVERY OF INCREMENT FROM NATURAL WATER, MG/L

LAB NO.	ANALYST NO.	INCREMENT, MG/L	AMPUL 5	AMPUL 6	AMPUL 7	AMPUL 8
101	1	0.1162	0.1352	0.8902	0.8102	
101	2	0.1142	0.1382	0.9902	0.8502	
102	3	0.1214	0.1314	0.9614	0.9114	
106	1	0.1061	0.1311	0.8561	0.7711	
106	2	0.1011	0.1311	0.8811	0.7811	
106	3	0.1111	0.1311	0.8911	0.7811	
107	3	0.1051	0.1341	0.9041	0.7941	
107	4	0.1091	0.1461	0.8941	0.7841	
110	1	0.1201	0.2161	0.8840	0.8200	
110	2	0.1321	0.2001	0.9600	0.8200	
110	3	0.1131	0.0641	0.6421	0.6781	
110	4	0.0841	0.1011	0.6921	0.7711	
110	5	0.0921	0.1291	0.8000	0.7000	
110	6	0.1141	0.1541	0.8051	0.7151	
112	1FW	0.1050	0.1450	0.8530	0.7710	
112	1EW	0.1210	0.1540	0.9640	0.8260	
113	3	0.2510R	0.3820	0.8160	0.9090	
113	4	0.1390	0.1610	0.8780	0.7990	
114	1	0.1198	0.1678	1.0048	0.8098	
115	1	0.1426	0.1656	0.9446	0.8646	
116	1	0.1101	0.1291	0.8951	0.7931	
117	1	0.2162R	0.2162	1.0062	1.4062R	
120	1	-0.1501	0.0166	0.7663	0.4144	
121	1	0.0943	0.1333	0.8503	0.8373	
122	1	0.1063	0.1343	0.8273	0.7153	
123	1	0.1222	0.1482	0.8702	0.8602	
123	2	0.1212	0.1312	0.8742	0.9182	
125	4	0.0992	0.1312	0.8902	0.7002	
126	2	0.1111	0.1471	0.9581	0.8361	
126	3	0.1272	0.1482	1.4071R	0.9661	
127	2	0.0848	0.2088	0.8708	0.7808	
127	1	0.1540	0.1840	0.6690	0.6290	
134	1	0.1053	0.1503	0.7683	0.6603	

FW = FRESH WATER
EW = ESTUARINE WATER

R = REJECTED

APPENDIX 2

Summary of Data

Recoveries from Distilled Water

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS
NITROGEN - AMMONIA, AMPUL 2

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER
INCREMENT = 0.21

N 26 RANGE 0.21 VARIANCE 0.32000 COEF. VAR. 0.33047
TRUE VAL. 0.21 STD. DEV. 0.00617 SKEWNESS 1.43663
MEAN 0.23769 CONF. LIM. 0.07855 NO. OF CELLS 6
MEDIAN 0.21500 PERCENT, RELATIVE TO TRUE VALUE.
ACCURACY 4.96018

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.13
0.15
0.15
0.18
0.19
0.19
0.19
0.20
0.20
0.21
0.21
0.21
0.21
0.22
0.23
0.23
0.24
0.24
0.25
0.26
0.27
0.34
0.35
0.44
0.45

HISTOGRAM

CELL MID. FREQ.
0.1300 3
0.1940 11
0.2580 8
0.3219 2
0.3859 0
0.4499 2

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS
NITROGEN - AMMONIA, AMPUL 1

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER
INCREMENT = 0.26

N 26 RANGE 0.40000 COEF. VAR. 0.34471
TRUE VAL. 0.26 VARIANCE 0.00740 1.16502
MEAN 0.24961 STD. DEV. 0.08604 6
MEDIAN 0.24500 CONF. LIM. (95%) 0.16864
ACCURACY -8.00007 PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.11
0.14
0.16
0.16
0.18
0.19
0.20
0.20
0.20
0.23
0.23
0.24
0.24
0.25
0.25
0.25
0.26
0.26
0.26
0.27
0.27
0.28
0.31
0.32
0.38
0.41
0.51

HISTOGRAM

CELL MID. FREQ.
0.1100 2
0.1899 7
0.2699 13
0.3499 2
0.4299 1
0.5099 1

METHOD AND PERFORMANCE EVALUATION, AQCL, HQD
METHOD STUDY 2, NUTRIENTS

NITROGEN - AMMONIA, AMPUL 3

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 1.71

N 26 RANGE 0.68999 COEF. VAR. 0.10853
TRUE VAL. 1.71 VARIANCE 0.03647 SKENNESS 1.13301
MEAN 1.75961 STD. DEV. 0.19098 NO. OF CELLS 6
MEDIAN 1.70000 CONF. LIM (95%) 0.37432
ACCURACY 2.90138 PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

1.54
1.55
1.56
1.60
1.60
1.61
1.61
1.62
1.66
1.66
1.68
1.68
1.69
1.69
1.71
1.72
1.72
1.73
1.75
1.77
1.78
1.89
1.98
2.10
2.10
2.11
2.23

HISTOGRAM

CELL MID. FREQ.
1.5400 5 XXXX
1.6779 12 XXXXXXXXXXXX
1.8159 3 XXX
1.9539 2 XX
2.0919 3 XXX
2.2299 1 X

METHOD AND PERFORMANCE EVALUATION, AQCL, HQD
METHOD STUDY 2, NUTRIENTS

NITROGEN - AMMONIA, AMPUL 4

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 1.92

N 26 RANGE 1.02000 COEF. VAR. 0.14079
TRUE VAL. 1.92 VARIANCE 0.07864 SKENNESS 1.66525
MEAN 1.99192 STD. DEV. 0.28044 NO. OF CELLS 6
MEDIAN 1.90000 CONF. LIM (95%) 0.54968
ACCURACY 3.74589 PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

1.68
1.73
1.76
1.80
1.80
1.81
1.82
1.85
1.86
1.86
1.88
1.88
1.89
1.90
1.90
1.90
1.94
1.96
1.96
1.98
2.01
2.10
2.10
2.24
2.65
2.69
2.70

HISTOGRAM

CELL MID. FREQ.
1.6800 3 XXX
1.8840 16 XXXXXXXXXXXXXXXX
2.0880 3 XXX
2.2920 1 X
2.4960 0
2.7000 3 XXX

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - NITRATE, AMPUL 1

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.16

N 28 RANGE 0.12000 COEF. VAR. 0.21726
TRUE VAL. 0.16 VARIANCE 0.00088
MEAN 0.13714 STD. DEV. 0.02879 SKENNESS 0.08573
MEDIAN 0.14000 CONF. LIM. (95%) 0.05839 NO. OF CELLS 6
ACCURACY -14.28581 PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.08
0.09
0.10
0.10
0.10
0.10
0.11
0.12
0.12
0.12
0.12
0.12
0.12
0.13
0.14
0.14
0.14
0.14
0.14
0.15
0.15
0.16
0.16
0.16
0.16
0.16
0.16
0.18
0.19
0.20

HISTOGRAM

CELL MID. FREQ.
0.0800 2 XX
0.1040 4 XXXX
0.1279 6 XXXXX
0.1519 13 XXXXXXXXXXXXX
0.1759 1 X
0.1999 2 XX

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - NITRATE, AMPUL 2

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.19

N 28 RANGE 0.26999 COEF. VAR. 0.28411
TRUE VAL. 0.19 VARIANCE 0.00262 SKENNESS 1.54482
MEAN 0.18035 STD. DEV. 0.05124 NO. OF CELLS 6
MEDIAN 0.18000 CONF. LIM. (95%) 0.10043
ACCURACY -8.77204 PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.10
0.10
0.10
0.12
0.12
0.13
0.13
0.14
0.14
0.16
0.16
0.16
0.16
0.17
0.17
0.18
0.18
0.18
0.18
0.18
0.19
0.19
0.19
0.19
0.19
0.20
0.20
0.20
0.21
0.22
0.22
0.24
0.37

HISTOGRAM

CELL MID. FREQ.
0.1000 4 XXXX
0.1539 12 XXXXXXXXXXXXX
0.2079 10 XXXXXXXXXXXXX
0.2619 1 X
0.3159 0
0.3699 1 X

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - NITRATE, AMPUL 4

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 1.08

N 29 TRUE VAL. 1.08 RANGE 1.08999 COEF. VAR. 0.18008
MEAN 1.17241 VARIANCE 0.04457 SKEWNESS 2.31939
MEDIAN 1.11000 STD. DEV. 0.21113 NO. OF CELLS 6
CONF. LIM. (95%) 0.41381
ACCURACY 6.54995 PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.92
0.97
0.98
1.00
1.00
1.03
1.04
1.06
1.06
1.08
1.10
1.10
1.11
1.11
1.11
1.12
1.12
1.14
1.19
1.21
1.22
1.24
1.24
1.28
1.31
1.32
1.40
1.53
2.01

HISTOGRAM

CELL MID. FREQ.

0.9200 5 XXXXX
1.1380 18 XXXXXXXXXXXXXXXXXX
1.3559 4 XXXX
1.5739 1 X
1.7919 0
2.009, 1 X

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - NITRATE, AMPUL 3

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 1.24

N 29 TRUE VAL. 1.24 RANGE 0.79000 COEF. VAR. 0.13664
MEAN 1.26792 VARIANCE 0.03001 SKEWNESS 1.82445
MEDIAN 1.23000 STD. DEV. 0.17325 NO. OF CELLS 6
CONF. LIM. (95%) 0.33957
ACCURACY 0.95569 PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

1.08
1.08
1.10
1.10
1.10
1.13
1.13
1.16
1.18
1.19
1.20
1.21
1.21
1.22
1.22
1.23
1.23
1.24
1.25
1.26
1.28
1.30
1.30
1.31
1.31
1.46
1.47
1.65
1.87

HISTOGRAM

CELL MID. FREQ.

1.0600 6 XXXXX
1.2380 18 XXXXXXXXXXXXXXXXXX
1.3960 3 XXX
1.540 0
1.720 1 X
1.8700 1 X

METHOD AND PERFORMANCE EVALUATION, ACCL, HQD
METHOD STUDY 2, NUTRIENTS

PHOSPHATE - SOL., ORTHO, AMPUL 2

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.038

N	29	RANGE	0.0300	COEFF. VAR.	0.19753
TRUE VAL.	0.038	VARIANCE	0.00004	SKENNESS	-0.31361
MEAN	0.03531	STD. DEV.	0.00697	NO. OF CELLS	6
MEDIAN	0.03600	CONF. LIM. (95%)	0.01366		
ACCURACY	-7.07813	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.020
0.020
0.024
0.028
0.030
0.030
0.031
0.032
0.032
0.033
0.034
0.035
0.035
0.035
0.036
0.037
0.037
0.038
0.038
0.038
0.040
0.040
0.040
0.041
0.044
0.048
0.050

HISTOGRAM

CELL MID.	FREQ.
0.0200	2 XX
0.0260	2 XX
0.0319	7 XXXXX
0.0379	14 XXXXXXXXXXXXX
0.0439	2 XX
0.0499	2 XX

METHOD AND PERFORMANCE EVALUATION, ACCL, HQD
METHOD STUDY 2, NUTRIENTS

PHOSPHATE - SOL., ORTHO, AMPUL 1

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.029

N	29	RANGE	0.05999	COEFF. VAR.	0.40213
TRUE VAL.	0.029	VARIANCE	0.00011	SKENNESS	2.23827
MEAN	0.02672	STD. DEV.	0.01074	NO. OF CELLS	6
MEDIAN	0.02600	CONF. LIM. (95%)	0.02105		
ACCURACY	-13.17740	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.010
0.010
0.017
0.019
0.019
0.020
0.021
0.021
0.022
0.025
0.025
0.026
0.026
0.026
0.027
0.028
0.028
0.028
0.028
0.030
0.030
0.030
0.030
0.046
0.070

HISTOGRAM

CELL MID.	FREQ.
0.0100	2 XX
0.0219	14 XXXXXXXXXXXXX
0.0339	11 XXXXXXXXXXXXX
0.0459	1 X
0.0579	0
0.0699	1 X

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

PHOSPHATE - SOL., CATH., AMPUL 3

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.333

TRUE VAL. 29 RANGE 0.09000 COEF. VAR. 0.05108
MEAN 0.37465 STD. DEV. 0.01913 SKEWNESS -1.35700
MEDIAN 0.37800 CONF. LIM. (95%) 0.37740 NO. OF CELLS 6
ACCURACY -1.57602 PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.310
0.347
0.350
0.352
0.357
0.359
0.364
0.365
0.370
0.372
0.374
0.375
0.376
0.377
0.378
0.380
0.380
0.383
0.384
0.386
0.390
0.392
0.393
0.398
0.400
0.400

HISTOGRAM

CELL MID. FREQ.
0.300 1 X
0.380 0
0.460 3 XXX
0.540 6 XXXXX
0.620 14 XXXXXXXXXXXXX
0.700 5 XXXXX

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

PHOSPHATE - SOL., ORTHO, AMPUL 4

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.335

TRUE VAL. 29 RANGE 0.06000 COEF. VAR. 0.04107
MEAN 0.33089 STD. DEV. 0.00018 SKEWNESS 0.08756
MEDIAN 0.33000 CONF. LIM. (95%) 0.02664 NO. OF CELLS 6
ACCURACY -1.22504 PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.300
0.310
0.310
0.320
0.320
0.320
0.320
0.320
0.320
0.320
0.330
0.330
0.330
0.330
0.330
0.332
0.332
0.332
0.336
0.340
0.340
0.340
0.340
0.342
0.350
0.360
0.360

HISTOGRAM

CELL MID. FREQ.
0.3000 1 X
0.3119 2 XX
0.3239 6 XXXXX
0.3359 16 XXXXXXXXXXXXXXXXX
0.3479 2 XX
0.3599 2 XX

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - KJELD., TGT., AMPUL 5

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.31

N	33	RANGE	0.77999	COEF. VAR.	0.56265
TRUE VAL.	0.31	VARIANCE	0.04644	SKENNESS	0.51385
MEAN	0.38302	STD. DEV.	0.21551	NO. OF CELLS	6
MEDIAN	0.34000	CONF. LIM. (95%)	0.42240		
ACCURACY	23.55806	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.04
0.10
0.10
0.10
0.14
0.14
0.16
0.16
0.16
0.19
0.21
0.28
0.30
0.30
0.31
0.32
0.32
0.32
0.34
0.34
0.35
0.35
0.41
0.41
0.42
0.44
0.47
0.47
0.54
0.54
0.59
0.61
0.62
0.76
0.78
0.80
0.82

HISTOGRAM

CELL MID.	FREQ.
0.0400	3
0.1959	6
0.3519	13
0.5079	4
0.6639	3
0.8199	4

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - KJELD., TGT., AMPUL 6

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.20

N	33	RANGE	0.61000	COEF. VAR.	0.58907
TRUE VAL.	0.20	VARIANCE	0.02373	SKENNESS	0.34918
MEAN	0.26151	STD. DEV.	0.15405	NO. OF CELLS	6
MEDIAN	0.24000	CONF. LIM. (95%)	0.30194		
ACCURACY	30.75743	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.00
0.02
0.05
0.06
0.10
0.10
0.10
0.10
0.10
0.10
0.19
0.19
0.20
0.22
0.22
0.23
0.23
0.23
0.24
0.24
0.25
0.25
0.29
0.29
0.30
0.32
0.33
0.34
0.40
0.40
0.43
0.43
0.45
0.50
0.57
0.61

HISTOGRAM

CELL MID.	FREQ.
0.0000	4
0.1219	4
0.2439	14
0.3659	5
0.4879	4
0.6100	2

METHOD AND PERFORMANCE EVALUATION, ACCL, HQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - KJELD., TOT., AMPUL 8

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 4.61

N	33	RANGE	7.09000	COEF. VAR.	0.31434
TRUE VAL.	4.61	VARIANCE	1.00033	SKEWNESS	-0.75609
MEAN	4.37151	STD. DEV.	1.37416	NO. OF CELLS	6
MEDIAN	4.60000	CONF. LIM. (95%)	2.69335		
ACCURACY	-2.27777	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.10
2.29
2.35
2.56
2.56
2.95
3.40
3.50
4.08
4.44
4.50
4.50
4.50
4.55
4.57
4.58
4.60
4.66
4.68
4.70
4.71
4.72
4.72
4.80
4.80
4.98
5.00
5.45
6.10
6.26
6.74
7.19

HISTOGRAM

CELL MID.	FREQ.
0.1000	1 X
1.5179	0
2.9359	7 XXXXXX
4.3540	20 XXXXXXXXXXXXXXXXXX
5.7719	3 XXX
7.1899	2 XX

METHOD AND PERFORMANCE EVALUATION, ACCL, HQO
METHOD STUDY 2, NUTRIENTS

NITROGEN - KJELD., TOT., AMPUL 7

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 4.10

N	34	RANGE	6.13000	COEF. VAR.	0.30464
TRUE VAL.	4.10	VARIANCE	1.82717	SKEWNESS	-0.96105
MEAN	3.92146	STD. DEV.	1.35464	NO. OF CELLS	6
MEDIAN	4.07000	CONF. LIM. (95%)	2.34189		
ACCURACY	-1.85591	PERCENT, RELATIVE TO TRUE VALUE.			

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.03
2.10
2.16
2.36
2.45
2.75
2.90
2.90
3.76
3.78
3.84
3.97
4.00
4.00
4.01
4.02
4.06
4.08
4.12
4.20
4.20
4.22
4.26
4.30
4.35
4.42
4.47
4.80
4.95
5.23
5.30
5.44
5.74
6.16

HISTOGRAM

CELL MID.	FREQ.
0.0300	1 X
1.2560	0
2.4819	7 XXXXXX
3.7079	16 XXXXXXXXXXXXXXXXXX
4.6340	8 XXXXXXX
6.1599	2 XX

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

PHOSPHORUS - TOTAL, AMPUL 5

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.110

N	TRUE VAL.	MEAN	MEAN	RANGE	VARIANCE	STD. DEV.	CONF. LIM.	COEF. VAR.	SKEWNESS	NO. OF CELLS
35	0.11262	0.11000	0.11000	0.06399	0.00022	0.01499	0.02938	0.13314	0.68862	6
ACCURACY 0.60594 PERCENT, RELATIVE TO TRUE VALUE.										

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

HISTOGRAM	CELL MID.	FREQ.
	0.0860	3 XXX
	0.0988	6 XXXXX
	0.1115	15 XXXXXXXXXXXXX
	0.1243	7 XXXXXXX
	0.1371	2 XX
	0.1499	2 XX

METHOD AND PERFORMANCE EVALUATION, ACCL, WQO
METHOD STUDY 2, NUTRIENTS

PHOSPHORUS - TOTAL, AMPUL 6

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.132

N	TRUE VAL.	MEAN	MEAN	RANGE	VARIANCE	STD. DEV.	CONF. LIM.	COEF. VAR.	SKEWNESS	NO. OF CELLS
35	0.13137	0.13200	0.13200	0.06800	0.00018	0.01367	0.02679	0.10406	0.41610	6
ACCURACY -1.14797 PERCENT, RELATIVE TO TRUE VALUE.										

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

HISTOGRAM	CELL MID.	FREQ.
	0.1020	2 XX
	0.1156	7 XXXXX
	0.1292	18 XXXXXXXXXXXXX
	0.1428	4 XXXX
	0.1563	3 XXX
	0.1699	1 X

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS
PHOSPHORUS - TOTAL, AMPUL 7

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.882

N	TRUE VAL.	COEF. VAR.	SKEWNESS	NO. OF CELLS
36	0.862	0.64199	0.13895	6
MEAN	0.85080	0.01397	-1.44883	
MEDIAN	0.88000	0.11822		
ACCURACY	-2.51507	CONF. LIM. (95%)	0.20171	

PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.452
0.597
0.606
0.665
0.706
0.800
0.805
0.829
0.833
0.840
0.840
0.850
0.855
0.863
0.876
0.880
0.884
0.890
0.892
0.893
0.900
0.908
0.909
0.911
0.920
0.923
0.925
0.940
0.940
0.948
1.094

HISTOGRAM

CELL MID.	FREQ.
0.4520	1 X
0.5603	2 XX
0.7087	2 XX
0.8571	19 XXXXXXXXXXXXXXXXXX
0.9155	11 XXXXXXXXXXXXXXXXXX
1.0739	1 X

METHOD AND PERFORMANCE EVALUATION, AQCL, WQO
METHOD STUDY 2, NUTRIENTS
PHOSPHORUS - TOTAL, AMPUL 8

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 0.772

N	TRUE VAL.	COEF. VAR.	SKEWNESS	NO. OF CELLS
35	0.772	0.33600	0.08377	6
MEAN	0.77971	0.00426	0.17784	
MEDIAN	0.78000	0.06532		
ACCURACY	0.40416	CONF. LIM. (95%)	0.12803	

PERCENT, RELATIVE TO TRUE VALUE.

RECOVERY OF INCREMENT

DATA IN
ASCENDING
ORDER

0.625
0.654
0.678
0.685
0.720
0.735
0.747
0.750
0.750
0.750
0.758
0.760
0.760
0.770
0.775
0.778
0.780
0.783
0.788
0.790
0.790
0.799
0.800
0.800
0.807
0.810
0.810
0.810
0.820
0.840
0.870
0.883
0.894
0.961

HISTOGRAM

CELL MID.	FREQ.
0.6250	2 XX
0.6922	3 XXX
0.7594	17 XXXXXXXXXXXXXXXXXX
0.8265	9 XXXXXXXXXX
0.8937	3 XXX
0.9609	1 X